CLAIMS <u>DETAILED DESCRIPTION</u> <u>TECHNICAL FIELD</u> <u>PRIOR ART</u> EFFECT OF THE INVENTION <u>TECHNICAL PROBLEM</u> <u>MEANS</u> <u>EXAMPLE</u> <u>DESCRIPTION OF DRAWINGS</u> <u>DRAWINGS</u> <u>CORRECTION</u> or <u>AMENDMENT</u>

[Translation done.]

CLAIMS

[Claim(s)]
[Claim 1] The active material of the non-sintering positive electrode for alkaline batteries where it belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system, it has the layer structure, and the spacing of the (003) field is 5.5-7.0A, and a cobalt average valence is characterized by consisting of a high order cobalt oxide which made the principal component the gamma-oxy-cobalt hydroxide defined by being size, and a solid-solution particle which made nickel hydroxide the principal component rather than 3.0.
[Claim 2] It belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system, it has the layer structure, and the spacing of the (003) field is 5.5-7.0A. And the high order cobalt oxide with which the cobalt average valence made the principal component the gamma-oxy-cobalt hydroxide which was defined by being size and contained K+ or Na+ in the crystal further rather than 3.0, The active material of the non-sintering positive electrode for alkaline batteries characterized by consisting of solid-solution particles which made nickel hydroxide the principal component.
[Claim 3] The aforementioned gamma-oxy-cobalt hydroxide is the active material of the non-sintering positive electrode for alkaline batteries according to claim 2 characterized by containing 20-33-mol% K+ inside a crystal to a cobalt atom.
[Claim 4] The aforementioned gamma-oxy-cobalt hydroxide is the active material of the non-sintering positive electrode for alkaline batteries according to claim 2 characterized by containing 20-33-molNa[% of]+ inside a crystal to a cobalt atom.
[Claim 5] The amount of the high order cobalt oxide which made the aforementioned gamma-oxy-cobalt hydroxide the principal component is the active material of the non-sintering positive electrode for alkaline batteries according to claim 2 characterized by being 2 - 10 % of the weight to the amount of the solid-solution particle which made nickel hydroxide the principal component.
[Claim 6] The cobalt oxide which is the nickel hydroxide solid-solution particle which has the enveloping layer of a cobalt oxide, and forms the enveloping layer is the active material of the non-sintering positive electrode for alkaline batteries where it belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system, it has the layer structure, and the spacing of the (003) field is 5.5-7.0A, and a cobalt average valence is characterized by being the high order cobalt oxide which made the principal component the gamma-oxy-cobalt hydroxide defined by being size rather than 3.0.
[Claim 7] The aforementioned enveloping layer is the active material of the non-sintering positive electrode for alkaline batteries according to claim 6 characterized by for the mean particle diameter of the nickel hydroxide solid-solution particle which has the enveloping layer of the aforementioned cobalt oxide being 5-20 micrometers, and the thickness having covered the whole particle surface with 0.2 micrometers or less.
[Claim 8] The cobalt oxide which is the nickel hydroxide solid-solution particle which has the enveloping layer of a cobalt oxide, and forms the enveloping layer It belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system, it has the layer structure, and the spacing of the (003) field is 5.5-7.0A. And the active material of the non-sintering positive electrode for alkaline batteries where a cobalt average valence is characterized by being the high order cobalt oxide which made the principal component the gamma-oxy-cobalt hydroxide which was defined by being size and contained K+ or Na+ in the crystal further rather than 3.0.
[Claim 9] The aforementioned enveloping layer is the active material of the non-sintering positive electrode for alkaline batteries according to claim 8 characterized by for the mean particle diameter of the nickel hydroxide solid-solution particle which has the enveloping layer of the aforementioned cobalt oxide being 5-20 micrometers, and the thickness having covered the whole particle surface with 0.2 micrometers or less.
[Claim 10] The aforementioned cobalt oxide is the active material of the non-sintering positive electrode for alkaline batteries according to claim 8 characterized by containing 20-33-mol% K+ inside a crystal to a cobalt atom.
[Claim 11] The aforementioned cobalt oxide is the active material of the non-sintering positive electrode for alkaline

batteries according to claim 8 characterized by containing 20-33-molNa[% of]+ inside a crystal to a cobalt atom.

[Claim 12] The active material of the non-sintering positive electrode for alkaline batteries where it is the nickel hydroxide solid-solution particle which has the enveloping layer of a cobalt oxide, and the cobalt average valence of the cobalt oxide which the spectral reflectance of the visible whole region (wavelength of 400-700nm) in the colorimetry using the diffuse reflection method is 3.5% or more, and has the maximal value of 4.0% or more of spectral reflectances in the wavelength of about (indigo) 450nm further, and forms an enveloping layer is characterized by being size rather than 3.0.

[Claim 13] The aforementioned enveloping layer is the active material of the non-sintering positive electrode for alkaline batteries according to claim 12 characterized by for the mean particle diameter of the nickel hydroxide solid-solution particle which has the enveloping layer of the aforementioned cobalt oxide being 5-20 micrometers, and the thickness having covered the whole particle surface with 0.2 micrometers or less.

[Claim 14] The aforementioned cobalt oxide is the active material of the non-sintering positive electrode for alkaline batteries according to claim 12 characterized by containing 20-33-mol% K+ inside a crystal to a cobalt atom.

[Claim 15] The aforementioned cobalt oxide is the active material of the non-sintering positive electrode for alkaline batteries according to claim 12 characterized by containing 20-33-molNa[% of]+ inside a crystal to a cobalt atom.

[Claim 16] The alkaline battery to which it belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system, it has the layer structure, and the spacing of the (003) field is 5.5-7.0A, and a cobalt average valence serves as a non-sintering positive electrode equipped with the active material which consisted of a high order cobalt oxide which made the principal component the gamma-oxy-cobalt hydroxide defined by being size, and a solid-solution particle which made nickel hydroxide the principal component, a negative electrode, and separator from 3.0 from the alkali electrolytic solution.

[Claim 17] It belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system, it has the layer structure, and the spacing of the (003) field is 5.5-7.0A. And the high order cobalt oxide with which the cobalt average valence made the principal component the gamma-oxy-cobalt hydroxide which was defined by being size and contained K+ or Na+ in the crystal further rather than 3.0, The alkaline battery which serves as a non-sintering positive electrode equipped with the active material which consisted of solid-solution particles which made nickel hydroxide the principal component, a negative electrode, and separator from the alkali electrolytic solution.

[Claim 18] The aforementioned gamma-oxy-cobalt hydroxide is an alkaline battery according to claim 17 characterized by containing 20-33-mol% K+ inside a crystal to a cobalt atom.

[Claim 19] The aforementioned gamma-oxy-cobalt hydroxide is an alkaline battery according to claim 17 characterized by containing 20-33-molNa[% of]+ inside a crystal to a cobalt atom.

[Claim 20] The amount of the high order cobalt oxide which made the aforementioned gamma-oxy-cobalt hydroxide the principal component is an alkaline battery according to claim 17 characterized by being 2 - 10 % of the weight to the amount of the solid-solution particle which made nickel hydroxide the principal component.

[Claim 21] The alkaline battery to which it belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system, it has the layer structure, and the spacing of the (003) field is 5.5-7.0A, and a cobalt average valence serves as a non-sintering positive electrode which made the subject the nickel hydroxide solid-solution particle by which the front face was covered with the high order cobalt oxide which made the principal component the gamma-oxy-cobalt hydroxide defined by being size rather than 3.0, a negative electrode, and separator from the alkali electrolytic solution.

[Claim 22] The aforementioned enveloping layer is an alkaline battery according to claim 21 characterized by for the mean particle diameter of the nickel hydroxide solid-solution particle which has the enveloping layer of the aforementioned cobalt oxide being 5-20 micrometers, and the thickness having covered the whole particle surface with 0.2 micrometers or less.

[Claim 23] It belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system, it has the layer structure, and the spacing of the (003) field is 5.5-7.0A. And a cobalt average valence is defined by being size rather than 3.0. The alkaline battery which serves as a non-sintering positive electrode which made the subject the nickel hydroxide solid-solution particle by which the front face was covered with the high order cobalt oxide which made the principal component the gamma-oxy-cobalt hydroxide which furthermore contained K+ or Na+ in the crystal, a negative electrode, and separator from the alkali electrolytic solution.

[Claim 24] The aforementioned enveloping layer is an alkaline battery according to claim 23 characterized by for the mean particle diameter of the nickel hydroxide solid-solution particle which has the enveloping layer of the, aforementioned cobalt oxide being 5-20 micrometers, and the thickness having covered the whole particle surface with 0.2 micrometers or less.

[Claim 25] The aforementioned cobalt oxide is an alkaline battery according to claim 23 characterized by containing 20-33-mol% K+ inside a crystal to a cobalt atom.

[Claim 26] The aforementioned cobalt oxide is an alkaline battery according to claim 23 characterized by containing

20-33-molNa[% of]+ inside a crystal to a cobalt atom.

[Claim 27] The alkaline battery to which the spectral reflectance of the visible whole region (wavelength of 400-700nm) in the colorimetry using the diffuse reflection method serves as a non-sintering positive electrode where it had the maximal value of 4.0% or more of spectral reflectances in the wavelength of about (indigo) 450nm, and the cobalt average valence made the subject the nickel hydroxide solid-solution particle covered with the cobalt oxide which is size rather than 3.0, a negative electrode, and separator from the alkali electrolytic solution at 3.5% or more.

[Claim 28] The aforementioned enveloping layer is an alkaline battery according to claim 27 characterized by for the mean particle diameter of the nickel hydroxide solid-solution particle which has the enveloping layer of the aforementioned cobalt oxide being 5-20 micrometers, and the thickness having covered the whole particle surface with 0.2 micrometers or less.

[Claim 29] The aforementioned cobalt oxide is an alkaline battery according to claim 27 characterized by containing 20-33-mol% K+ inside a crystal to a cobalt atom.

[Claim 30] The aforementioned cobalt oxide is an alkaline battery according to claim 27 characterized by containing 20-33-molNa[% of]+ inside a crystal to a cobalt atom.

[Claim 31] The manufacture method of the non-sintering positive active material for alkaline batteries characterized by providing the following. The 1st process made into the humid particle to which the alkaline-water solution was dropped at this and the particle front face got wet with the alkaline-water solution while mixing the nickel hydroxide solid-solution particle with the enveloping layer of cobalt hydroxide within the container equipped with the microwave heating means and the mixed stirring means. The 2nd process which makes the inside of this container airtight, continues mixture, mainly heating microwave irradiation and carries out the temperature up of the aforementioned humid particle to predetermined temperature. The 3rd process which dispel an airtight and air is made to flow in a container after reaching predetermined temperature, and continues mixture, controlling the aforementioned microwave output so that particle temperature becomes fixed, and draws the aforementioned humid particle to a bone dry.

[Claim 32] The manufacture method of the non-sintering positive active material for alkaline batteries according to claim 31 characterized by equipping the internal-surface portion of the aforementioned container with the heating means, and heating a container internal surface auxiliary by the aforementioned heating means between the 1st process of the above, and the 3rd process.

[Claim 33] This particle is the manufacture method of the non-sintering positive active material for alkaline batteries according to claim 31 that the mean particle diameter of the nickel hydroxide solid-solution particle with the enveloping layer of the aforementioned cobalt hydroxide is 5-20 micrometers, as for the aforementioned enveloping layer, the thickness has covered the whole particle surface with 0.2 micrometers or less, and it is characterized by a BET specific surface area being 5-12m2/g.

[Claim 34] The heating temperature in the 2nd process of the above and the 3rd process is the manufacture method of the non-sintering positive active material for alkaline batteries according to claim 31 characterized by being 90-130 degrees C.

[Claim 35] It is the manufacture method of the positive active material for alkaline batteries according to claim 31 which the aforementioned alkaline-water solution is the solution of KOH or NaOH, and the concentration is size from 40 % of the weight, and is characterized by the drip being a range from which the weight ratio of the alkali solute to the dry weight of a nickel hydroxide solid-solution particle with the enveloping layer of cobalt hydroxide becomes 4 - 6%.

[Translation done.]
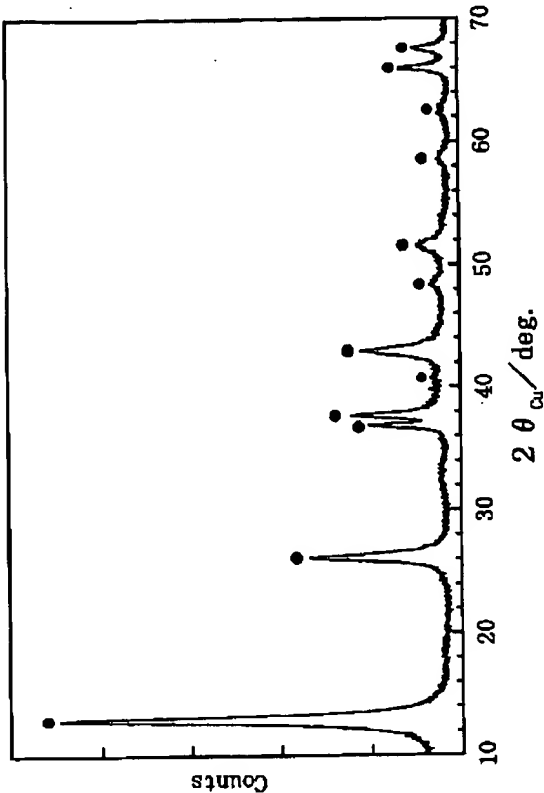
[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] Especially this invention relates to the active material and its manufacture method of the non-sintering positive electrode for alkaline batteries which consists of the solid-solution particle and cobalt oxide electric conduction agent which make nickel hydroxide a principal component in relation to an alkaline battery.
[0002]
[Description of the Prior Art] In recent years, as for the alkaline battery, high capacity-ization is strongly demanded with the spread of pocket devices. Especially a nickel-hydrogen battery is a rechargeable battery which consists of a positive electrode which consists of an active material which made nickel hydroxide the subject, and a negative electrode which made the hydrogen storing metal alloy the main material, and is spreading quickly as a highly reliable rechargeable battery in high capacity.
[0003] Hereafter, the positive electrode for these alkaline batteries is explained. As a positive electrode for alkaline batteries, it divides roughly and there are two, a sintering formula and non-sintering. The former sinks nickel salt solutions, such as nickel nitrate solution, into the porosity nickel sintered carrier of about 80% of porosity which was made to sinter a core material and nickel powder, such as a punching metal, and was obtained, then sinks into it at an alkaline-water solution, in a porosity nickel sintered carrier, makes nickel hydroxide generate and is manufactured. Since this positive electrode is difficult to enlarge the porosity of a substrate more than this, the amount of active materials with which it fills up cannot be increased, but there is a limitation in high capacity-ization.
[0004] Moreover, as a latter non-sintering positive electrode, as indicated by JP,50-36935,A, what is filled up with a nickel hydroxide particle is proposed by the foaming porous-body substrate of 95% or more of porosity which consists of a nickel metal and which continued in three dimensions, and it is widely used for it as a positive electrode of the alkaline battery of amount-on-hand capacity, for example. In this non-sintering positive electrode, it is made that bulk density is filled up with a spherical large nickel hydroxide particle from a viewpoint of high-capacity-izing. Moreover, it is common to make a part of metal ions, such as cobalt, cadmium, and zinc, dissolve to the above-mentioned nickel hydroxide particle, and to use for it for improvement in an electric discharge property, or charge acceptance nature and a life property. Although the pore (pore) size of a foaming porous-body substrate is about 200-500 micrometers here, and a charge-and-discharge reaction advances smoothly by the nickel hydroxide particle near [where current collection was maintained] the substrate skeleton in order to fill up this pore with the spherical nickel hydroxide whose particle size is several micrometers - dozens of micrometers, the reaction of a nickel hydroxide particle which is separated from a skeleton does not fully progress. Therefore, in the non-sintering positive electrode, in order to raise the utilization factor of the nickel hydroxide particle with which it was filled up, an electric conduction agent is used and between nickel hydroxide particles is connected electrically.
[0005] As this electric conduction agent, although metal simple substances, such as cobalt and nickel, may be used, in many cases, a divalent cobalt oxide like cobalt hydroxide and 1 cobalt oxide is used. Although a cobalt oxide divalent [these] does not have conductivity in itself, it oxidizes electrochemically to the beta-oxy-cobalt hydroxide which has conductivity in charge of the first stage within a cell, and this is considered to function effectively as an electric conduction network. By existence of this electric conduction network, it becomes possible to raise sharply the utilization factor of the active material with which it was filled up with high density, and high capacity-ization is attained in a non-sintering positive electrode compared with a sintering formula positive electrode.
[0006] However, also in the non-sintering positive electrode of the above composition, the conductive ability of the electric conduction network was not perfect, and there was an upper limit in the utilization factor of a nickel hydroxide particle. In the electrochemical oxidation reaction in the above cells, this is because a divalent cobalt oxide cannot be completely changed to beta-oxy-cobalt hydroxide. When the case where cobalt hydroxide is used for an electric conduction agent is described as an example, although it is dependent also on pH and temperature at the time of the

composition, the cobalt hydroxide which added and compounded the alkaline-water solution in divalent cobalt salt solution, such as a cobalt sulfate, a cobalt nitrate, and a cobalt chloride, has generally high crystallinity, and its size of a microcrystal is large. It dissolves in the electrolytic solution of a strong base within a cell, this cobalt hydroxide forms cobalt complex ion (HCoO2-), and this oxidizes to beta-oxy-cobalt hydroxide by early charge. However, since the generation concentration in the inside of the electrolytic solution of this complex ion is very as small as hundreds of ppm, the cobalt hydroxide of most which was added all over the positive electrode receives oxidization not according to the reaction which went via this complex ion but according to solid phase reaction. In the cobalt hydroxide which consists of a big microcrystal as mentioned above at this time, since there are few reacting points at the time of oxidization (reaction which draws out an electron and a proton from cobalt hydroxide), oxidization does not fully advance to the interior of a crystal. Therefore, although it changes with conditions of an initial charge etc., it leaves many unreacted cobalt hydroxide which generally does not have conductivity inside a crystal, the conductive ability of an electric conduction network becomes imperfect, and a limitation arises in a positive-electrode utilization factor.
[0007] Furthermore, when the overdischarge of the cell was carried out, or it was left in the state of the short circuit or saved under the mothball or the elevated temperature, there was a fault that positive-electrode capacity fell in the above-mentioned positive electrode. Under such conditions, since positive-electrode potential is kept lower than the usual electric discharge end state, the reduction reaction of the cobalt oxide which contained the beta-oxy-cobalt hydroxide which forms an electric conduction network simultaneously with deeper electric discharge (reduction) of a nickel hydroxide particle also advances. Under the present circumstances, the active material which is in the position distant from the substrate skeleton for the imperfection of the conductive ability of the above electric conduction networks is left without the ability being able to discharge, a reduction reaction advances intensively only in the section near the substrate skeleton with current-collection nature, and it is completely returned to divalent, and the cobalt oxide near the skeleton is eluted in the electrolytic solution as cobalt complex ion, and is diffused to the active material section of a position which is separated from a nickel substrate skeleton. By the nickel-hydrogen battery which used the hydrogen storing metal alloy for the negative electrode, since the inside of a cell is maintained at a strong hydrogen-reduction atmosphere, reduction and lytic reaction of above-mentioned cobalt advance in acceleration, and also concurs with the phenomenon (that is, it never returns to a positive electrode) in which the cobalt complex ion eluted further deposits as metal cobalt in a negative-electrode side. For this reason, in the above-mentioned positive electrode, an electric conduction network is destroyed and capacity falls.
[0008] Recent years come and some meanses to improve the imperfection of the above positive-electrode electric conduction networks are reported. First, by raising the oxidization degree of a divalent cobalt oxide, as approach which improves above imperfection, the cobalt hydroxide in a positive active material is heated under coexistence with an alkaline-water solution and oxygen (air), and the technique of oxidizing to a cobalt oxide with a larger valence than divalent [to which the crystal structure was confused] is indicated by JP,8-148145,A (or USP No. 5,629,111 specification) etc. In this official report, the cell property which used it is indicated to be oxidization to the cobalt oxide of about 2.9 **s. As a content similar to this, improvement of the cobalt oxide to 2.5 - 2.93 ** is described in JP,9-147905,A.
[0009] On the other hand, the point of giving the above-mentioned heat-treatment to the nickel hydroxide solid-solution particle (henceforth a Co(OH) 2 covering nickel particle) which has the enveloping layer of cobalt hydroxide is also described by aforementioned JP,8-148145,A. A Co(OH) 2 covering nickel particle stirs a nickel hydroxide solid-solution particle in the solution of divalent cobalt salt here. How (liquid phase process) to adjust pH and to deposit cobalt hydroxide on a particle front face while alkali is dropped, Or it is what is produced by the method (machine alligation) of adding cobalt hydroxide powder to a nickel hydroxide solid-solution particle, and making it covering a particle front face with cobalt hydroxide using an operation of the shearing force by machine mixture, or impulse force etc. It was widely known as a means which raises the cobalt dispersibility in the inside of a positive electrode for many years. When the above-mentioned heat-treatment is given to such a Co(OH) 2 covering nickel particle, the effect of that the dispersibility of cobalt is high and the interface of a nickel hydroxide solid-solution particle and an enveloping layer being joined at the time of processing can obtain the positive active material which brings about a quite good electric conduction network conjointly in the state with few amounts of cobalt to be used.
[0010] Moreover, the method of heating, while making the Co(OH) 2 covering nickel particle containing the alkaline-water solution flow in fluidized-bed-granulation equipment etc. as the manufacture method of a positive active material which was described above or making it distribute is shown in JP,9-73900,A. According to this method, there is an advantage, like generating of the particle lump at the time of processing can be lessened.
[0011]
[Problem(s) to be Solved by the Invention] However, advance of oxidization of cobalt hydroxide changes with the concentration of the alkali component which exists in the circumference, temperature (temperature of goods) of a particle a delicate moisture condition of a particle, and own [at the time of processing], surrounding humidity, oxygen

densities, etc. a lot, and a complicated reaction path exists. Therefore, it is very difficult to suppress completely the phenomenon of cobalt hydroxide fully not oxidizing to the meant state, or a by-product generating. For this reason, the cobalt average valence of the cobalt oxide in the above-mentioned official report had stopped by about 2.9 on parenchyma. Although possibility that a cobalt valence will be in a state a little higher than this is also considered by oxidization at the time of cell initial charge etc. within an actual cell, such an oxide is still before [cell composition] inferior in electronic-conduction nature compared with the cobalt oxide with which a valence exceeds 3.0. Therefore, the electric conduction network of the positive electrode using this was hard to be called sufficient thing, and the room of improvement was left behind.

[0012] this invention tends to aim at improvement in a utilization factor of the further positive active material, improvement in an overdischarge-proof property as a cell, etc. by solving the above technical problems and using the high order cobalt oxide with which the average valence made the principal component gamma-oxy-cobalt hydroxide higher enough than 3.0 for an electric conduction agent.

[0013]
[Means for Solving the Problem] In order to solve the above-mentioned technical problem, this invention belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system. The high order cobalt oxide with which it has the layer structure, and the spacing of the (003) field is 5.5-7.0A, and the average valence of cobalt made the principal component the gamma-oxy-cobalt hydroxide defined by being size rather than 3.0, It is related with the active material of the non-sintering positive electrode for alkaline batteries which consists of solid-solution particles which made nickel hydroxide the principal component, and the alkaline battery using this. Furthermore, this invention also shows simultaneously the above-mentioned efficient manufacture method of a positive active material.

[0014] The alkaline battery [after neglect in an overdischarge or the short circuit state, and long-term preservation or the preservation under an elevated temperature] which can maintain high capacity can be offered being able to produce the sintering formula positive electrode for alkaline batteries with the electric conduction network based on the high conductivity of gamma-oxy-cobalt hydroxide, and attaining a very high utilization factor according to this invention.

[0015]
[Embodiments of the Invention] It belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system, it has the layer structure, and the spacing of the (003) field is 5.5-7.0A, and invention according to claim 1 is the active material of the non-sintering positive electrode for alkaline batteries where the average valence of cobalt consists of solid-solution particles which made the principal component the high order cobalt oxide which made the principal component the gamma-oxy-cobalt hydroxide defined by being size, and nickel hydroxide rather than 3.0.

[0016] gamma-oxy-cobalt hydroxide is a high order oxide obtained in divalent cobalt hydroxide by oxidizing violently under KOH or NaOH, water, and the coexistence atmosphere of air (oxygen) here. Since conductive ability is superior to the cobalt oxide (mixed state of beta-oxy-cobalt hydroxide and a divalent cobalt oxide) obtained by the electrochemical oxidation reaction in the conventional cell, and the cobalt oxide (almost equal to beta-oxy-cobalt hydroxide in crystal structure) of about 2.9 **s obtained by well-known alkali coexistence air oxidation, gamma-oxy-cobalt hydroxide raises the electric discharge utilization factor of nickel hydroxide. Moreover, for [this] high conductivity, the time of an overdischarge or short circuit preservation can also maintain current collection from much nickel hydroxide, and gamma-oxy-cobalt hydroxide delays advance of the intensive reduction reaction in said section near the substrate skeleton. In addition, since the reduction potential in the inside of the alkali electrolytic solution is ** compared with beta-oxy-cobalt hydroxide etc. while gamma-oxy-cobalt hydroxide has oxidized to the state with very high order itself, the state (state which cobalt may dissolve into the electrolytic solution) of 2.0 ** is not returned easily. By the above reason, degradation of the positive-electrode capacity in an overdischarge, the time of short circuit preservation, etc. can be suppressed further.

[0017] A claim 2 belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system, it has the layer structure, and the spacing of the (003) field is 5.5-7.0A. And the high order cobalt oxide with which the cobalt average valence made the principal component the gamma-oxy-cobalt hydroxide which was defined by being size and contained K+ or Na+ in the crystal further rather than 3.0, It is the active material of the non-sintering positive electrode for alkaline batteries which consists of solid-solution particles which made nickel hydroxide the principal component.

[0018] A claim 3 is characterized by gamma-oxy-cobalt hydroxide containing 20-33-mol% K+ inside a crystal to a cobalt atom, and a claim 4 is characterized by gamma-oxy-cobalt hydroxide containing 20-33-molNa[% of]+ inside a crystal to a cobalt atom. There are two sorts (the crystal structure from which all serve as a skeleton is equal), the type containing K+ and the type containing Na+, in gamma-oxy-cobalt hydroxide, and it is guessed from an ideal structure expression that the mole fraction of M/Co (it is here and M is either K or Na) is 33%. However, since the oxide equivalent to ideal structure is rarely obtained, it has a range about the above on parenchyma.

[0019] A claim 5 is characterized by being 2 - 10 % of the weight to the amount of the solid-solution particle to which

the amount of the high order cobalt oxide which made gamma-oxy-cobalt hydroxide the principal component made nickel hydroxide the principal component. The current collection from a solid-solution particle cannot be kept nice as too little [the amount of a high order oxide] than this, the amount of nickel hydroxide can become less relatively with it being excessive, and the positive electrode of high-energy density cannot be produced. Therefore, as for the amount of a high order cobalt oxide, it is desirable that it is in the aforementioned range.

[0020] It is the nickel hydroxide solid-solution particle which has the enveloping layer which consists of a cobalt oxide, the cobalt oxide of the enveloping layer belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system, and the claim 6 has the layer structure, and the spacing of the (003) field is 5.5-7.0A, and it is characterized by a cobalt average valence being the high order cobalt oxide which made the principal component the gamma-oxy-cobalt hydroxide defined by being size from 3.0.

[0021] The mean particle diameter of the nickel hydroxide solid-solution particle which has the enveloping layer of a cobalt oxide is 5-20 micrometers, and the enveloping layer of a claim 7 is the active material of the non-sintering positive electrode for alkaline batteries according to claim 6 where the thickness is characterized by having covered the whole particle surface with 0.2 micrometers or less. If there is no mean particle diameter of a solid-solution particle within the limits of the above, the positive electrode of high-energy density cannot be given for the reasons of a fall of bulk density etc. Moreover, if the thickness of an enveloping layer exceeds 0.2 micrometers, there cannot be too many amounts of the cobalt oxide occupied to the whole active material, the amount of nickel hydroxide can become less relatively, and the positive electrode of high-energy density cannot be given too. within the limits of the above [the thickness of a mean particle diameter and an enveloping layer] -- it is -- in addition -- and in order to make current collection capacity from nickel hydroxide into the maximum, that with which the enveloping layer covered the whole particle surface completely is the most desirable as an active material particle

[0022] A claim 8 is a nickel hydroxide solid-solution particle which has the enveloping layer of a cobalt oxide. the cobalt oxide of the enveloping layer It belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system, it has the layer structure, and the spacings of the (003) field are 5.5-7.0. And rather than 3.0, a cobalt average valence is defined by being size, and is characterized by being the high order cobalt oxide which made the principal component the gamma-oxy-cobalt hydroxide which contained K+ or Na+ in the crystal further.

[0023] The mean particle diameter of the nickel hydroxide solid-solution particle which has the enveloping layer which consists of a cobalt oxide is 5-20 micrometers, and a claim 9 is the active material of the non-sintering positive electrode for alkaline batteries according to claim 8 characterized by the enveloping layer having covered the whole particle surface with the thickness of 0.2 micrometers or less. A claim 10 is the active material of the non-sintering positive electrode for alkaline batteries according to claim 8 where a cobalt oxide is characterized by containing 20-33-mol% K+ inside a crystal to a cobalt atom, and is the active material of the non-sintering positive electrode for alkaline batteries according to claim 8 where a claim 11 is characterized by a cobalt oxide containing 20-33-molNa[% of]+ inside a crystal to a cobalt atom.

[0024] A claim 12 is a nickel hydroxide solid-solution particle which has the enveloping layer which consists of a cobalt oxide, and the spectral reflectance of the visible whole region (wavelength of 400-700nm) in the colorimetry using the diffuse reflection method is 3.5% or more, and it has the maximal value of 4.0% or more of spectral reflectances in the wavelength of about (indigo) 450nm further, and the cobalt average valence of an enveloping layer is characterized by being size rather than 3.0. The cobalt oxide which the color of an active material particle is closely connected with the electronic state of the cobalt oxide which forms an enveloping layer here, and presents the above colors has very high electronic-conduction nature. This is because the electronic state (existence of a tetravalent cobalt kind) with the above-mentioned color higher order than 3.0 ** peculiar to gamma-oxy-cobalt hydroxide is reflected.

[0025] The mean particle diameter of the nickel hydroxide solid-solution particle which has the enveloping layer of a cobalt oxide is 5-20 micrometers, and the enveloping layer of a claim 13 is the active material of the non-sintering positive electrode for alkaline batteries according to claim 12 where the thickness is characterized by having covered the whole particle surface with 0.2 micrometers or less. A claim 14 is the active material of the non-sintering positive electrode for alkaline batteries according to claim 12 where a cobalt oxide is characterized by containing 20-33-mol% K+ inside a crystal to a cobalt atom, and is the active material of the non-sintering positive electrode for alkaline batteries according to claim 12 where a claim 15 is characterized by a cobalt oxide containing 20-33-molNa[% of]+ inside a crystal to a cobalt atom.

[0026] A claim 16 belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system. The high order cobalt oxide with which it has the layer structure, and the spacing of the (003) field is 5.5-7.0A, and the average valence of cobalt made the principal component the gamma-oxy-cobalt hydroxide defined by being size rather than 3.0, It is the alkaline battery which serves as a non-sintering positive electrode equipped with the active material which consisted of solid-solution particles which made nickel hydroxide the principal component, a negative electrode, and separator from the alkali electrolytic solution.

[0027] A claim 17 belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system. It has the layer structure and the spacing of the (003) field is 5.5-7.0A. And the high order cobalt oxide with which the average valence of cobalt made the principal component the gamma-oxy-cobalt hydroxide which was defined by being size and contained K+ or Na+ in the crystal further rather than 3.0, It is the alkaline battery which serves as a non-sintering positive electrode equipped with the active material which consisted of solid-solution particles which made nickel hydroxide the principal component, a negative electrode, and separator from the alkali electrolytic solution.

[0028] A claim 18 is an alkaline battery according to claim 17 to which gamma-oxy-cobalt hydroxide is characterized by containing 20-33-mol% K+ inside a crystal to a cobalt atom, and is an alkaline battery according to claim 17 to which a claim 19 is characterized by gamma-oxy-cobalt hydroxide containing 20-33-molNa[% of]+ inside a crystal to a cobalt atom.

[0029] Moreover, a claim 20 is an alkaline battery according to claim 17 to which the amount of the high order cobalt oxide which made gamma-oxy-cobalt hydroxide the principal component is characterized by being 2 - 10 % of the weight to the amount of the solid-solution particle which made nickel hydroxide the principal component. A claim 21 is an alkaline battery, and it belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system, and has the layer structure, and the spacing of the (003) field is 5.5-7.0A, and a cobalt average valence serves as a non-sintering positive electrode which made the subject the nickel hydroxide solid-solution particle covered with the high order cobalt oxide which made the principal component the gamma-oxy-cobalt hydroxide defined by being size, a negative electrode, and separator from 3.0 from the alkali electrolytic solution.

[0030] The mean particle diameter of the nickel hydroxide solid-solution particle which has the enveloping layer of a cobalt oxide is 5-20 micrometers, and the aforementioned enveloping layer of a claim 22 is an alkaline battery according to claim 21 to which the thickness is characterized by having covered the whole particle surface with 0.2 micrometers or less. A claim 23 is an alkaline battery and belongs to hexagonal, a prismatic crystal, and one of monoclinic system crystal system. It has the layer structure and the spacing of the (003) field is 5.5-7.0A. And a cobalt average valence is defined by being size rather than 3.0. It becomes the non-sintering positive electrode which made the subject the nickel hydroxide solid-solution particle covered with the high order cobalt oxide which made the principal component the gamma-oxy-cobalt hydroxide which furthermore contained K+ or Na+ in the crystal, a negative electrode, and separator from the alkali electrolytic solution.

[0031] The mean particle diameter of the nickel hydroxide solid-solution particle which has the enveloping layer of a cobalt oxide is 5-20 micrometers, and a claim 24 is an alkaline battery according to claim 23 characterized by the thickness of the enveloping layer having covered the whole particle surface with 0.2 micrometers or less. A claim 25 is an alkaline battery according to claim 23 to which a cobalt oxide is characterized by containing 20-33-mol% K+ inside a crystal to a cobalt atom, and is an alkaline battery according to claim 23 to which a claim 26 is characterized by a cobalt oxide containing 20-33-molNa[% of]+ inside a crystal to a cobalt atom.

[0032] The spectral reflectance of the visible whole region (wavelength of 400-700nm) in the colorimetry which used the diffuse reflection method is 3.5% or more, and a claim 27 is an alkaline battery which serves as a non-sintering positive electrode which made the subject the nickel hydroxide solid-solution particle which has the maximal value of 4.0% or more of spectral reflectances in the wavelength of about (indigo) 450nm and, by which the cobalt average valence was covered with the cobalt oxide which is size rather than 3.0, a negative electrode, and separator from the alkali electrolytic solution.

[0033] The mean particle diameter of the nickel hydroxide solid-solution particle which has the enveloping layer of a cobalt oxide is 5-20 micrometers, and the aforementioned enveloping layer of a claim 28 is an alkaline battery according to claim 27 to which the thickness is characterized by having covered the whole particle surface with 0.2 micrometers or less. A claim 29 is an alkaline battery according to claim 27 to which a cobalt oxide is characterized by containing 20-33-mol% K+ inside a crystal to a cobalt atom, and is an alkaline battery according to claim 27 to which a claim 30 is characterized by a cobalt oxide containing 20-33-molNa[% of]+ inside a crystal to a cobalt atom.

[0034] Within the container which a claim 31 is the manufacture method of the non-sintering positive active material for alkaline batteries, and was equipped with the microwave heating means and the mixed stirring means Mixing a nickel hydroxide solid-solution particle (Co(OH) 2 covering nickel particle) with the enveloping layer of cobalt hydroxide The 1st process made into the humid particle to which the alkaline-water solution was dropped at this and the particle front face got wet with the alkaline-water solution, The 2nd process which makes the inside of this container airtight, continues mixture, mainly heating microwave irradiation and carries out the temperature up of the aforementioned humid particle to predetermined temperature, After reaching predetermined temperature, dispel an airtight and air is made to flow in a container, mixture is continued, controlling the aforementioned microwave output so that particle temperature becomes fixed, and it consists of the 3rd process which draws the aforementioned humid particle to a bone dry.

[0035] Here, when oxidizing a Co(OH) 2 covering nickel particle in the coexistence atmosphere of an alkaline-water

solution, the following two processes can be considered as a reaction mechanism of the cobalt hydroxide which forms an enveloping layer. Cobalt hydroxide dissolves as cobalt complex ion (HCoO2-) by the reaction of (a formula 1) into the alkaline-water solution which exists in a particle enveloping layer front face, and the 1st process oxidizes by the reaction of (a formula 2) because this touches oxygen, and it deposits on a particle as a high order cobalt oxide.
[0036]
[Formula 1]
Co (OH) 2+OH-->HCoO2-+H2O (lytic reaction) [0037]
[Formula 2]
HCoO2-+1/2H2O+1 / 4O2 ->CoOOH+OH- (oxidization / deposit reaction) While cobalt hydroxide generates water in the atmosphere with which alkali and oxygen coexist (formula 3), it oxidizes in solid phase reaction like (that is, ** which is not accompanied by the dissolution), and the 2nd process becomes a high order cobalt oxide. (A formula 4) shows consumption of the oxygen in this atmosphere.
[0038]
[Formula 3]
Co(OH)2+OH-->CoOOH+H2 O+e- (solid phase oxidation reaction) [0039]
[Formula 4] 1/4O2+1/2H2 O+e-->OH - Although the product was written as CoOOH (form tops are 3.0 **) in the still more nearly above-mentioned formula since it was simple, it can oxidize even to gamma-oxy-cobalt hydroxide higher order than 3.0 ** by controlling a reaction well. In this case, although the outline of a reaction does not change, a reaction formula becomes a little more complicated than the above.
[0040] If the above two processes are considered in detail, the 1st advance of a process will be dependent on the solubility (formula 1) to the alkaline-water solution of cobalt hydroxide first. However, for example in about 60 degrees C, it does not pass over this solubility to hundreds of ppm in KOH solution of 30 % of the weight of concentration, and a dissolution rate is not so large, either. Therefore, in order to raise a reaction rate, it is necessary to make atmosphere into an elevated temperature. However, if liquid evaporates and a dryness exhaustion is carried out by the reasons nil why surrounding humidity is too low etc. when it is made an elevated temperature here, generation of the complex ion of (a formula 1) will become impossible, and a reaction will stop. On the other hand, in oxidation reaction of (a formula 2), it is important that the produced cobalt complex ion fully touches oxygen (air), and if it becomes an elevated temperature in the environment where circumference oxygen runs short, conductive scarce Co 3O4 (Co valence : 2.67) will generate according to the following side reaction of (a formula 5).
[0041]
[Formula 5]
HCoO2-+1/6O2 ->1/3Co3O4+OH- (side reaction 1) Although it is the 2nd process, a high order cobalt oxide generates according to a mechanism that cobalt hydroxide is heated under alkali coexistence (formula 3). At this time, under oxygen coexistence, the reaction of (a formula 4) occurs simultaneously and the reaction of (a formula 3) advances continuously. In order to advance this reaction smoothly, it becomes the point to make the system of reaction into an elevated temperature, to make OH-concentration high (formula 3), to make O2 concentration high (formula 4), and to remove the generated water from the system of reaction moderately. here -- removal of water -- superfluous -- becoming (that is, it being made to dry too much) -- the reaction for generation of OH-ion from an alkali kind becoming impossible (formula 3) stops Moreover, conversely, if removal of water becomes inadequate, since O2 concentration near the cobalt hydroxide falls relatively, (a formula 4) will not fully progress, but the side reaction of (a formula 6) will occur instead of (a formula 3) as a result.
[0042]
[Formula 6]
Co(OH)2+2/3OH- ->1/3Co3O4+4/3H2O+2/3e- (side reaction 2) Even if it considers which process as mentioned above, it is clear that the water at the time of processing and the state of oxygen (air) carry out important work. You have to process controlling the amount of water and oxygen by the bottom of an elevated temperature well to the particle which became FANIKYURA (damp or wet condition with [are the classification on chemical engineering, and liquid fully exists in the particle front face, and] permeability) by having the alkaline-water solution of optimum dose in a front face, in order to advance most efficiently oxidization in the alkali coexistence atmosphere of a Co(OH) 2 covering nickel particle, considering this viewpoint.
[0043] Then, in invention according to claim 31, it is the 1st process first, and it can be made the humid particle of a uniform FANIKYURA state by dropping an alkaline-water solution, mixing a Co(OH) 2 covering nickel particle. The microwave heating in the 2nd-3rd continuing process is technique which gives vibration to a dielectric (it is an alkaline-water solution in this case) on molecule level by microwave irradiation to a humid particle, and is heated with a collision and frictional heat of a molecule. In the 2nd process, the temperature up of the humid particle can be quickly carried out to predetermined temperature, without producing most heating unevenness by performing microwave

heating, mixing under airtight atmosphere. Sending of the air which dispelled the airtight in the 3rd continuing process aims at supplying the oxygen of required sufficient amount to the system of reaction while it discharges efficiently the superfluous water generated by oxidation reaction of cobalt hydroxide out of a system. Under the present circumstances, although the latent heat of vaporization will be taken by evaporation of superfluous water, acting as the monitor of the particle temperature, by microwave heating, it compensates with heat and the temperature in a system is maintained at predetermined within the limits. If microwave irradiation is used as a heating means in the case of advance of oxidization, since heating of a particle will take place from the cobalt enveloping layer portion on the front face of a particle which has got wet with the alkaline-water solution, compared with other heating meanses, the oxidization efficiency of an enveloping layer portion becomes high, and the cobalt of an enveloping layer oxidizes completely to the state exceeding 3.0 **. Moreover, while the terminal point of this oxidation reaction cannot discriminate easily but water exists in the particle front face, a humid particle is drawn to a bone dry, because oxidization may progress further. If a particle is drawn to a bone dry, it can be said that processing is completed.

[0044] In the claim 32, the internal-surface portion of the aforementioned container is equipped with the heating means, and it is characterized by heating a container internal surface auxiliary by the aforementioned heating means from the 1st process to the 3rd process. Such heating is very effective when the water or alkali Myst which evaporated prevents dewing by the container internal surface, and a particle's adhering, or a particle condensing and solidifying.

[0045] A claim 33 is what specified the aforementioned Co(OH) 2 covering nickel particle, and the mean particle diameter is 5-20 micrometers, as for an enveloping layer, the thickness has covered the whole particle surface with 0.2 micrometers or less, and the aforementioned particle is characterized by a BET specific surface area being 5-12m2/g. For the reasons of a fall of the grain child bulk density which is not in above-mentioned within the limits etc., a mean particle diameter cannot give the positive electrode of high-energy density. When this becomes excessive also about the thickness of an enveloping layer, the amount of the nickel hydroxide which determines positive-electrode capacity will become less relatively, and it becomes impossible to give the positive electrode of high-energy density too. Moreover, in order to make easy to perform current collection from a nickel hydroxide mother particle, the state of an enveloping layer where the whole particle surface was covered is the most desirable. Furthermore, since the wettability of the grain child from whom this becomes [too little / excessive or] changes a lot about a BET specific surface area, it becomes difficult to make a particle result in a FANIKYURA state with a predetermined alkaline-water solution on the occasion of processing. The BET specific surface area of this viewpoint to a Co(OH) 2 covering nickel particle has the most desirable thing of above-mentioned within the limits.

[0046] A claim 34 is characterized by the heating temperature in the 2nd process of the above and the 3rd process being 90-130 degrees C. Although the speed of oxidation reaction is greatly influenced with temperature, advance of oxidization by setting temperature being less than 90 degrees C will be slow, and per one batch will also take several hours to it. Moreover, it is not desirable from being easy to produce adhesion of the particle in a container wall etc. simultaneously. On the other hand, at the temperature exceeding 130 degrees C, a reaction occurs too much violently and does an injury to the nickel hydroxide inside an enveloping layer. As for heating setting temperature, it is more desirable than the above viewpoint to consider as 90-130 degrees C.

[0047] The aforementioned alkaline-water solution is the solution of KOH or NaOH, and the concentration is size from 40 % of the weight, and a claim 35 is characterized by the drip being a range from which the weight ratio of the alkali solute to the dry weight of a Co(OH) 2 covering nickel particle becomes 4 - 6%. Since the oxidation reaction used by this invention occurs near the boiling point of an alkaline-water solution, the vapor rate of the water in an alkaline-water solution is large. However, as the 1st process of oxidation reaction of this invention, cobalt hydroxide dissolves in an alkaline-water solution, cobalt complex ion generates, and further, this complex ion reacts with oxygen and becomes a high order cobalt oxide. Therefore, on the occasion of processing, a certain amount of quantity of the alkaline-water solution must exist in the particle front face under an elevated temperature. When it puts in another way, even if it is an elevated temperature (the range of the processing temperature described in the claim 34), if evaporation of an alkaline-water solution is early, a reaction cannot fully be advanced. Since the boiling point rises and a vapor rate becomes slow so that the concentration of an alkaline-water solution is higher than this viewpoint, it can be said that it is suitable for processing. Moreover, when the 2nd oxidization process is considered, in order that, as for oxidization, the one where OH-concentration is higher may progress well from (a formula 3), the concentration of an alkaline-water solution has the good higher one too. As mentioned above, as for the concentration of the alkaline-water solution to be used, an adult thing is suitable from 40 % of the weight.

[0048] moreover, the amount of the above [making drip of alkali solution into the above-mentioned range] makes a humid particle result in a moderate FANIKYURA state -- most -- suitable -- **** -- in addition -- and it is because condensation (an alkali solute serves as [be / under / processing / reaction / it] a carbon dioxide in air with a carbonate, and this happens in order that this may work as a binder in the dryness process of a particle.) of a particle can be suppressed to the minimum If the drip of alkali solution becomes [too little] than this, oxidation reaction is imperfect,

and an unreacted part can be left, and on the other hand, an excessive grain child's condensation cannot become intense and cannot process smoothly.

[0049]

[Example] The example of this invention is explained in detail based on an experimental result below.

(Example 1)

1. Into the production sodium-hydroxide solution of a high order cobalt oxide, the cobalt-sulfate solution of 1 mol/l was added gradually, and it stirred, adjusting so that pH of solution may maintain 12 at 35 degrees C, and cobalt hydroxide was deposited. After rinsing this, the vacuum drying was carried out and it considered as the cobalt hydroxide standard sample. This cobalt hydroxide standard sample is beta. - It is scanning-electron-microscope (SEM) observation about it being the hexagon-head tabular particle of the size this sample of whose is about about 0.2 micrometers in X diffraction measurement about having the crystal structure (number of a JCPDS mineral-matter file : 30 -443) of type, and checked, respectively that the specific surface area of this sample was 25m2/g further by the BET adsorption method.

[0050] Next, the granular high-purity-water potassium-oxide reagent was ground under dryness atmosphere (inside of a dry box), and sufficient amount was mixed to the above-mentioned cobalt hydroxide standard sample. Then, the mixed sample was taken out out of the dry box, it put in in the 110-degree C heating container, and air was sent in. In this process, a mixed sample serves as the shape of FANIKYURA which contained the moisture in air a little for the deliquescence of a potassium hydroxide, and oxidization advances in connection with this. In this way, the sample was held within the heating container for 12 hours, and oxidation reaction was completed. After taking out the sample after that and fully rinsing, it was made to dry over 3 hours at 80 degrees C, and the high order cobalt oxide x of this invention was obtained. Moreover, except [all] using a granular high-purity-water sodium-oxide reagent instead of a potassium-hydroxide reagent, the same processing as the above was carried out and the high order cobalt oxide y of this invention was produced.

[0051] 2. The nickel hydroxide solid-solution particle used as the mother particle of the production positive electrode of of a positive electrode was compounded using the following well-known technique. That is, the nickel sulfate was made into the principal component, and while aqueous ammonia adjusted Solution pH in the solution which only the specified quantity made contain a cobalt sulfate and a zinc sulfate, sodium-hydroxide solution was dropped gradually, and the method of depositing a spherical nickel hydroxide solid-solution particle was used. The nickel hydroxide solid-solution particle which deposited here was rinsed, and it dried, and considered as the positive-electrode mother particle. In addition, the bulk density of this nickel hydroxide solid-solution particle was about 2.0g/cc, and the mean particle diameter was 10 micrometers.

[0052] Next, the 7.0 weight sections of the aforementioned high order cobalt oxide x and the pure water of a proper quantity are added to the 100 weight sections of the nickel hydroxide solid-solution particle obtained in this way, mixed distribution was carried out, and it considered as the active material slurry. The foaming nickel porous-body substrate with a% [of porosity] of 95 and a thickness of 1.3mm was filled up with this active material slurry, and it was made to dry within a 80-degree C dryer. It rolled out so that it might be thin to 0.7mm using a roll press after that. And cutting processing was carried out and this was made into the nickel positive electrode corresponding to the high order cobalt oxide x at the predetermined size.

[0053] It processed like [oxide / high order cobalt / y] the above, and the corresponding nickel positive electrode was produced. Furthermore, the 7.0 weight sections and pure water of the aforementioned cobalt hydroxide standard sample are added to the 100 weight sections of a nickel hydroxide solid-solution particle, mixed distribution was carried out, it considered as the active material slurry, and subsequent procedures produced the nickel positive electrode for comparison like the above-mentioned.

3. About three sorts of nickel positive electrodes produced by production of a cell, and the evaluation above of a positive electrode, the nickel-hydrogen battery of nominal capacity 1600mAh was respectively produced in 4 / 5A sizes by the well-known method using the separator which consists of a negative electrode which made the hydrogen storing metal alloy the subject, and a polypropylene fiber nonwoven fabric which performed hydrophilicity-ized processing, and the electrolytic solution which made the principal component the potassium hydroxide (7-8N). About each cell, it examined by the method of describing in ** of a degree, and **, and the utilization factor of each nickel positive electrode and the capacity recovery factor after short circuit preservation were evaluated.

[0054] ** The utilization factor above-mentioned three sorts of each cells were charged by charge rate 0.1CmA for 15 hours, and the capacity of 5 cycle repeat and 5 cycle eye was measured for the cycle made to discharge until a cell voltage is set to 1.0V by electric discharge rate 0.2CmA. In this way, the utilization factor of each nickel positive electrode was computed by carrying out division process of the measured cell capacity by the geometric capacity (value which multiplied the weight of the nickel hydroxide with which it was filled up all over the positive electrode by electric capacity 289 mAh/g when presupposing that one electron of nickel hydroxide reacts) of a positive electrode.

[0055] ** The capacity of 5 cycle repeat and 5 cycle eye was measured for the cycle made to discharge until it charges

by charge rate 1CmA first for 1.2 hours and a cell voltage is set to 1.0V by electric discharge rate 1CmA about the cell which evaluation of capacity recovery-factor ** after short circuit preservation ended. Then, this cell was short-circuited with the electric resistance of 1 ohm, and it saved for two weeks under 45-degree C atmosphere. The capacity of 5 cycle repeat and 5 cycle eye was measured for the cycle made to discharge until it charges by charge rate 1CmA again for 1.2 hours and a cell voltage is set to 1.0V by electric discharge rate 1CmA about the cell after preservation. From the above measurement result, the capacity recovery factor after the short circuit preservation in each nickel positive electrode was computed by carrying out division process of the value of the cell capacity after short circuit preservation by the cell capacity before short circuit preservation.

[0056] The evaluation result of each cell is shown for classifying according to the kind of positive-electrode additive (Table 1).

[0057]

[Table 1]

正極添加剤の種類	利用率 [％]	短絡保存後の容量回復率 [％]
コバルト酸化物 x	99.2	98.8
コバルト酸化物 y	99.4	98.6
水酸化コバルト	81.8	75.5

[0058] compared with the positive electrode for comparison which used the cobalt hydroxide standard sample, the high order cobalt oxide x of this invention and the positive electrode using y were boiled markedly, and showed the high utilization factor and the capacity recovery factor so that more clearly than this Then, in order to clarify these causes, it analyzed in detail about the above-mentioned high order cobalt oxide x and y.

4. The X diffraction view of the high order cobalt oxide x of the analysis 4.1. high order cobalt oxide x4.1.1. crystal structure of a high order cobalt oxide, a valence, and the analysis this invention of composition is shown in drawing 1 . K alpha rays of Cu were used for X line source here. As the mark was put all over drawing, angle-of-diffraction 2theta can check 12 peaks in the section to 70 degrees from 10 degrees. Then, qualitative analysis of the compound corresponding to these peak positions was carried out by reference from a JCPDS mineral-matter file. Consequently, although were registered as an oxide of cobalt and the thing applicable to inside did not exist, it turns out that it is quite well in agreement with the diffraction pattern of the gamma-oxy-nickel hydroxide (file number : 6 -75) well known as a high order oxide of nickel. here according to reference (being what was known well P.Oliva's and others J.Power Sources, 8 (1982)229- 255. etc.) in gamma-oxy-nickel hydroxide -- false -- it is the oxide which belongs to-like (a geometry ---like) at an about 6 way ** system, and has the layer structure, the grid is elongating to c shaft orientations compared with a beta- type hydroxide, and the valence of nickel has attained further higher order than 3.0 Moreover, it is also known well that this gamma-oxy-nickel hydroxide contains an alkali cation in a crystal.

[0059] It is there, then the following ways estimated the cobalt average valence of the high order cobalt oxide x. First, the high order cobalt oxide x of the specified quantity and ferrous-ammonium-sulfate:FeSO4(NH4)2SO4 were mixed, and this was dissolved in the concentrated hydrochloric acid. In this process, Co ion of a larger valence than divalent oxidizes Fe2+ ion to Fe3+ ion, and self is returned to Co2+. Next, the fixed quantity of the whole quantity of Co2+ in the obtained solution was carried out by ICP AEM (fixed quantity value 1), and the amount of Fe3+ previously produced in one side was calculated with the oxidation reduction titration using potassium permanganate solution (fixed quantity value 2). The value was 3.42 ** when the cobalt average valence of the high order cobalt oxide x was calculated from both value by calculation used as 2.0+(fixed quantity value 2)/(fixed quantity value 1).

[0060] Moreover, when dissolved the high order cobalt oxide x in a concentrated hydrochloric acid apart from a top, the ICP AEM about the obtained solution was carried out, K+ existed in this oxide and the content set molar quantity of a cobalt atom to 100, it checked that it was equivalent to about 28. The above analysis result suggests strongly that the high order cobalt oxide x will be what is equivalent to a "gamma- type" oxide so to speak if the same naming as the case of nickel is followed. Both show behavior extremely similar in crystallography -- only in 1, the atomic numbers differ, but the ionic radius is also similar, and cobalt and nickel have the crystal structure with the same, further divalent hydroxide. Then, this invention persons set to a cobalt oxide as well as a nickel oxide, and are gamma. - The

crystal structure of the high order oxide of type was interpreted as existing, and the high order cobalt oxide x was defined as "gamma-oxy-cobalt hydroxide." About this gamma-oxy-cobalt hydroxide, the layer structure (the array of the cobalt layer seen from c shaft orientations is the repeat structure of ABC) of hexagonal system is assumed, and it becomes a passage that a spacing and its index attachment are summarized (Table 2) about the field (hkl) whose intensity is six in which the angle of diffraction was greatly read mostly by accuracy among 12 peaks shown in <u>drawing 1</u> as an X diffraction view.

[0061]
[Table 2]

h	k	l	dobs(Å)	I/I0obs
0	0	3	6.85	100
0	0	6	3.42	35
1	0	1	2.43	20
1	0	2	2.39	25
1	0	5	2.10	22
1	1	0	1.42	18

[0062] 4.1.2. "anodic CoOOH (1)" P.Benson and others indicated the structure described in the consideration (Table 2) to investigation and it of the past reference to be in Electrochim.Acta and 9 (1964)275-280. as research on a cobalt electrode -- it is extremely similar to the product They defined the cobalt oxide which gives X diffraction peaks strong near 6.8A of spacings including "anodic CoOOH (1)" in this reference as "beta-CoOOH", and it proposed distinguishing from the conductive scarce oxide "CoHO2" obtained by smothering cobalt hydroxide etc. here -- "CoHO2" -- an oxide has a roppo-rhombohedral structure, c axial length at the time of taking a hexagonal unit lattice is 13.13A, and the spacing of c shaft orientations becomes 4.38A of 1/the 3 However, a classification (Electrochim.Acta, 11 (1966) 1079-1087.) of H.Bode and others widely accepted about the present nickel hydroxide and its oxide teaches. If cobalt is classified according to an adjustable form, you should name the high order cobalt oxide x described in "anodic CoOOH (1)" (Table 2) of the account of the point with which extension of the grid to c shaft orientations is accepted "gamma-CoOOH" (gamma-oxy-cobalt hydroxide).

[0063] As research of the cobalt additive of the non-sintering positive electrode for alkaline batteries, Oshitani and others showed that "alpha- type" which the spacing of c shaft orientations is elongating, and "beta- type" which is not elongated existed to divalent cobalt hydroxide like the classification of H.Bode and others in nickel hydroxide in the Yuasa time signal and 65 (1988) 28-40. And it reported that the cobalt oxide divalent [these] added all over the positive electrode functioned effectively [since it becomes the oxide whose spacing of c shaft orientations is it about 4.4A to oxidize by the initial charge and this has conductivity]. Although Oshitani and others called the oxide with the above-mentioned conductivity "beta-CoOOH" unlike above P.Benson and others, this naming has H.Bode's and others the classification and adjustment about nickel, and, also generally is accepted. That is, as a conventional general interpretation, "beta-CoOOH" points out the oxy-cobalt hydroxide which extension is not accepted in the spacing of c shaft orientations as compared with c axial length (4.65A) of beta-Co (OH) 2, and has conductivity. And this "beta-CoOOH" is the oxide (by the JCPDS file, it is CoO (OH), a notation, and number:7-169.) which ** P.Benson and others probably called "CoHO2." It is thought that the spacing of c shaft orientations is a thing with the same crystal structure as 4.384A, and is equivalent to a crystalline low thing.

[0064] CoO (OH) Conductivity is very a low as a crystalline high thing (this is called "CoHO2") is in P.Benson's and others report, since the becoming oxide is deficient in own electronic-conduction nature of a microcrystal. however -- if production conditions are adjusted and crystallinity is made low (if it is made the thing of the type get blocked and "beta-CoOOH [type]" is written) -- the microcrystal itself -- small -- a bird clapper -- ** -- conductivity is discovered for the interface between microcrystal-microcrystals (function as an electronic-conduction side) increasing conjointly The report of this point carried out electrochemistry oxidization of the crystalline low CoO(OH) (CoO which exists partly in recent years, for example, was reported by the collection of the 37th cell debate lecture summaries, and p371 (1996). in the alkali electrolytic solution, was obtained, and contains a part of Co(es) 3O4. "Beta-CoOOH" in which the electrochemistry behavior of) has conductivity in short is considered that charge-and-discharge behavior is shown.

[0065] 4.1.3. If the classification about the cobalt oxide (especially hydroxide) described more than the classification about the reaction of a cobalt oxide is learned and summarized in H.Bode's and others diagram, it will become like <u>drawing 2</u> . Three sorts of the divalent cobalt oxide 2 which the conventional non-sintering positive electrode for

alkaline batteries is sufficient as, and is used, i.e., alpha-Co, (OH), and beta-Co (OH)2, and CoO change to beta-Co (OH) 2 easily in the alkali electrolytic solution, when it causes a chemical change too by the reaction of ** again, although alpha-Co (OH) 2 does not show CoO in drawing 2 . Therefore, the place of a join office oxidizes according to the reaction of ** at the time of initial charge, and these change to beta-CoOOH which has conductivity. However, generally, since the microcrystal of above-mentioned beta-Co (OH) 2 is large, in the charge reaction of ** to which most advances in solid phase reaction, the reacting point at the time of oxidization (reaction which draws out an electron and a proton from cobalt hydroxide) will decrease, and the unreacted cobalt hydroxide which does not have conductivity inside a crystal also remains. (In addition, it is thought that it depends for this amount of survival on the size and ambient temperature of the charging current at the time of initial charge, and the conditions of electrolytic-solution composition further.) Although it is returned by the reaction of ** (electric discharge) and being dealt in the cobalt oxide containing beta-CoOOH formed in this way, this reduction reaction does not occur in the charge-and-discharge-potential region of the usual cell. Therefore, the cobalt oxide containing beta-CoOOH functions as an electric conduction network for advancing the charge and discharge of a nickel hydroxide particle smoothly.

[0066] It is thought that it was produced with the reaction path of ** in drawing 2 on the other hand since the high order cobalt oxide x (namely, gamma-CoOOH) in this invention was obtained by intense oxidization of beta-Co (OH) 2. In addition, it is surmised that the reaction path (** in drawing) which corresponds for setting on cobalt generally cannot take place easily although it is known for nickel hydroxide that gamma-NiOOH will generate easily by the surcharge of beta-NiOOH. This is because it is expected that very big energy is required in order to extend between this layer and for an alkali cation to invade in a crystal, since the CoO (OH) crystal which is the basic structure of beta-CoOOH has hydrogen bond strong between oxygen-oxygen compared with beta-NiOOH, and for cobalt to reach a higher order oxidation state. These points differ with cobalt and nickel.

[0067] Moreover, although not shown in drawing 2 , there are two more points which are different by the cobalt oxide and the nickel oxide, and solubility [as opposed to the dark alkali solution of a divalent cobalt oxide in one] and another are existence of Spinel structure Co 3O4 (4 oxidization 3 cobalt). About the former, although a divalent cobalt oxide is not so big solubility, it dissolves in dark alkali solution as cobalt complex ion:HCoO2-. However, this behavior cannot make it clear how much it is participating in reactions, such as ** in drawing 2 , **, and **. About the latter, Co 3O4 peculiar to a cobalt oxide is very stable thermodynamically. Therefore, depending on conditions, the flume gap which performs baking etc. at an elevated temperature also changes to Co 3O4, and Co 3O4 of a valence 2.67 generates easily the hydroxide shown in drawing 2 in oxidization of **, **, and **, and advance of the oxidization to a state higher order than it is barred. Thus, while a cobalt oxide and a nickel oxide can perform the classification which was considerably similar like drawing 2 , they also have some delicately different points.

[0068] Next, drawing 2 explains the experimental result described in above P.Benson's and others reference. The compound cobalt hydroxide which they made the starting material first is alpha-Co (OH) 2 clearly judging from being indicated as "blue", or its X diffraction result (spacing of c shaft orientations : 8.4A). And generation of "anodic CoOOH (1)" at the time of carrying out electrochemistry oxidation of this in KOH solution is equivalent to the reaction of **. Moreover, "anodic CoOOH (2)" which they showed is equivalent to that to which a part of beta-CoOOH and Co 3O4 were intermingled in gamma-CoOOH. The mechanism of such alpha->gamma can also generate gamma-CoOOH. However, since a certain amount of time is taken [after pouring in a cell] to perform an initial charge when alpha-Co (OH) 2 is added to the non-sintering positive electrode for alkaline batteries, the reaction of ** will progress in the meantime and the reaction of ** cannot occur easily. on the other hand -- them -- cobalt hydroxide -- KOH -- aqueous -- inside -- leaving it -- things -- having obtained -- " -- CoHO -- two -- " -- a starting material -- it is -- alpha-Co -- (-- OH --) -- two -- the reaction of ** -- beta-Co (OH) 2 -- becoming -- continuing -- the dissolved oxygen in liquid -- oxidization of ** -- progressing -- being generated . The observation result this is also indicated to be as change of the color of an oxide: Blue -> white -> peach -> tea corresponds to the brown of the blue of alpha-Co (OH) 2, the white of beta-Co (OH) 2 - pink, and CoHO2, respectively, and is considered to be a first infallible thing.

[0069] thus, all the behavior of a cobalt oxide (especially hydroxide) conventionally reported by the diagram shown in drawing 2 -- conflict -- there is nothing -- explanation attachment **** And the high order cobalt oxide x of this invention is gamma-CoOOH higher order than trivalent, and it turns out that this does not exist all over the conventional positive electrode for alkaline batteries.

4.1.4. The ** type of the crystal structure expected as gamma-oxy-cobalt hydroxide by consideration drawing 3 about the crystal structure is shown. It thought with the same crystal structure as gamma-oxy-nickel hydroxide fundamentally, and the reference about this was made reference. By drawing 3 , gamma-oxy-cobalt hydroxide belongs to an about 6 way crystal system in false, it is a cobalt oxide with the layer structure, and the grid is elongating it to c shaft orientations. The periodic array of the cobalt layer seen from c shaft orientations is the repeat of ABC, and if it sees by the packing of cobalt-oxygen-oxygen-cobalt, it will serve as repeat structure of ACCBAACBB. Therefore, if its attention is paid only to this, a rhombohedral unit lattice can also be taken in geometry. The opening produced among

six oxygen ion (or hydroxide ion) arranged in the shape of [in drawing 3] triangular prism The actual measurement of the spacing shown in (Table 2), and a general effective ionic radius : rCo=0.68A (trivalent-6 coordination : 0.685A and tetravalent-6 coordination : central value with 0.67A), If rO=1.25A (divalent-6 coordination : divalent-6 coordination of 1.26A and OH- : central value with 1.23A of O2-) is used, if a sphere with a radius of about 1.64A can be contained, it will estimate from geometrical calculation. And as the sphere of a dotted line showed all over drawing, the inside of this opening is partially occupied by potassium ion. He becomes and this is understood also from the size of the opening which effective ionic-radius rK=1.52A (notes: the value of octahedron 6 general coordination is substituted for it since most central value of triangular prism 6 coordination is not known) of a potassium estimated by calculation, or a near thing. Moreover, since a moisture child also has a size near this opening, it is further expected by a part of opening that the moisture child is also incorporated.

[0070] In addition, although the equivalent opening existed also in the position except the sphere of a dotted line having shown in drawing 3 geometrically in the crystal, since potassium ion etc. was not able to make clear the actually occupied position strictly, the opening position was shown in the range legible as a ** type view. Furthermore, it will be called monoclinic system if it will be called a prismatic crystal when it changes delicately like the state of the state which a axial length showed to the left of drawing 4 with occupancy into the crystal of the above potassium ion etc. although the ** type was shown as exact hexagonal structure without the distortion in drawing 3 to the right, and it shifts slightly 90 degrees like the state of the state of the drawing 5 left to the right in the degree of c axial angle. However, it is very difficult also about strict becoming [of this point] clear.

[0071] 4.1.5. In order to grasp the analysis of electrochemistry behavior, next the electrochemistry behavior of gamma-oxy-cobalt hydroxide, the high order cobalt oxide x was filled up with and pressed, it considered as the test electrode at the 1cmx1cm foaming nickel porous-body substrate which welded lead wire, and the cyclic voltammetry (valve flow coefficient) was measured on condition that the following.

[0072] Electrolytic solution: What added LiOH-H2O by the ratio of 40 g/l in KOH solution of 31 % of the weight of concentration (20-degree C specific gravity 1.31 g/l)

Counter electrode: Hydrogen storing metal alloy negative electrode (what was made to carry out charge and discharge combining another nickel hydroxide electrode beforehand, and was fully activated)

reference pole: -- Hg/HgO sweep condition: -- for +700mV (oxidization side) - -700mV (reduction side) after sweeping from immersing potential to +500mV -- operation Trace-speed ambient temperature of 1mV/second: 20-degree-C result is shown in drawing 6 . As a, b, and the sign were described, a big charge-and-discharge peak is observed. This shows that this oxide has high conductivity. In addition, the sharp oxidation current in an electropositive potential field is followed on the oxygen evolution on a test electrode rather than near +600mV. Thinking from said diagram, the reduction-current peak a in drawing 6 corresponds to the reduction (electric discharge) to alpha-cobalt hydroxide from gamma-oxy-cobalt hydroxide, and the oxidation-current peak b corresponds to the reverse oxidization (charge). The potential of the charge and discharge in this gamma/alpha system shifts in about 50-100mV and the **** direction compared with the system of conventional beta/beta. This is considered to be the same phenomenon as being known well about gamma-oxy-nickel hydroxide.

[0073] 4.2. The X diffraction view of the high order cobalt oxide y of the analysis this invention of the high order cobalt oxide y4.2.1. crystal structure, a valence, composition, and electrochemistry behavior is shown in drawing 7 . As the mark was put, angle-of-diffraction 2theta can check at least nine peaks from 10 degrees in the section to 70 degrees. Then, when the JCPDS mineral-matter file performed qualitative analysis of the compound corresponding to these peak positions, it was quite well in agreement with the diffraction pattern of Na0.6CoO2 (file number 30-1181). For this Na0.6CoO2, C.Fouassier and others is J.Solid. State The crystal structure of Na0.6CoO2 which is the compound shown in Chem. and 6 (1973)532-537., and belongs to the false hexagonal (strictly prismatic crystal) one which has the layer structure, and they took into consideration and presented to the array of a cobalt-oxygen layer: The array of ACCBAACBB of cobalt-oxygen-oxygen-cobalt is the same as that of what was shown in drawing 3 . Therefore, the high order cobalt oxide y has the structure of drawing 3 as basic structure.

[0074] Next, the average valence of the high order cobalt oxide y and the amount of the alkali-metal ion (it is Na+ in this case) to contain were measured by the same method as having been shown in 4.1.1. Consequently, the cobalt average valence of this oxide is 3.39 **, and it turns out that the content of the alkali-metal ion at the time of setting molar quantity of a cobalt atom to 100 is equivalent to about 31. If it judges from these values, the high order cobalt oxide y is not above Na0.6CoO2. He can understand this to above Na0.6CoO2 obtaining by baking with 4 oxidization 3 cobalt (Co 3O4) and a sodium peroxide (Na 2O2) also from the point completely acquired by the option that the high order cobalt oxide y makes beta-cobalt hydroxide start material. And the average valence and alkali-metal ion content of the high order cobalt oxide y are quite close to the value about the high order cobalt oxide x shown by 4.1.1.

[0075] Furthermore, in order to grasp the electrochemistry behavior of the high order cobalt oxide y, analysis by the cyclic voltammetry (valve flow coefficient) was performed on the same conditions as having been shown in 4.1.5. This

result is as being shown in drawing 8 , and this is the almost same charge-and-discharge behavior as the high order cobalt oxide x shown in drawing 6 . Such an experimental result means that the high order cobalt oxide y has high conductivity like the high order cobalt oxide x. Moreover, transfer of a proton means happening in reversible between the high order cobalt oxide y and the alkali electrolytic solution simultaneously, and it is shown that a proton exists in the high order cobalt oxide y. If it carries out from this viewpoint, the high order cobalt oxide y will be a kind of "oxy-cobalt hydroxide."

[0076] The above analysis result has proved strongly that it has almost same crystal structure, physical properties, and electrochemistry behavior if the high order cobalt oxide y removes the point that the distance between layers of c shaft orientations differs for a while, as compared with the high order cobalt oxide x. That is, it is suitable for calling the high order cobalt oxide y "gamma-oxy-cobalt hydroxide." Then, this invention persons caught the high order oxide y as it is a kind of gamma-oxy-cobalt hydroxide, and they defined this as "Na type gamma-oxy-cobalt hydroxide." About this Na type gamma-oxy-cobalt hydroxide, the same layer structure as drawing 3 is assumed, and it becomes a passage that a spacing and its index attachment (thing at the time of presupposing that it is hexagonal) are summarized Table 2 Similarly (Table 3) comparatively about the field whose intensity is six in which the angle of diffraction was greatly read mostly by accuracy among nine peaks shown in drawing 7 as an X diffraction view.

[0077]

[Table 3]

h	k	l	dobs($\mathring{A}$)	I/I0obs
0	0	3	5.57	100
0	0	6	2.78	10
1	0	1	2.42	19
1	0	2	2.35	32
1	0	5	1.97	20
1	1	0	1.41	13

[0078] 4.2.2. Consider the crystal structure of the consideration about the crystal structure, next Na type gamma-oxy-cobalt hydroxide. Drawing 3 already explained that are the cobalt oxide which gamma-oxy-cobalt hydroxide belongs to an about 6 way ** system in false in 4.1.4., and has the layer structure, and the grid is developing to c shaft orientations, that the packing of the cobalt-oxygen-oxygen-cobalt seen from c shaft orientations in this case was the repeat of ACCBAACBB, etc. Then, if the radius of the opening produced among six oxygen ion (or hydroxide ion) arranged in the shape of triangular prism is estimated by geometrical calculation about Na type gamma-oxy-cobalt hydroxide based on the effective ionic radius used in the spacing shown in (Table 3), or 4.1.4., it will become about 1.15A. the sodium of this value is effective -- about [ionic-radius rNa=1.16A (6 coordination) and] -- I am doing one and the inside of an opening is occupied by sodium ion

[0079] In addition, although drawing 3 showed the ** type as exact hexagonal structure without distortion, as 4.1.4. already described, this structure may change with delicate change of a axial length or the degree of c axial angle to a prismatic crystal or monoclinic system structure. Although it has not performed this detailed becoming clear, probably it is guessed that the difference in the intensity ratio of the X diffraction peak of drawing 1 and drawing 7 (that is, difference of I/I0obs between (Table 2) and (Table 3)) is a thing reflecting the above-mentioned point. Furthermore, it is thought that the spacing of the field (003) of gamma-oxy-cobalt hydroxide is fundamentally governed strongly by the size of the alkali cation which occupies the inside of an opening so that more clearly than the calculation result and the above-mentioned calculation result which were shown by 4.1.4.

[0080] 5. As Relation above was Carried Out to Physical Properties and Positive-Electrode Property of Gamma-Oxy-Cobalt Hydroxide If the high order cobalt oxide x of this invention and y are summarized in the meaning which all give beta-oxy-cobalt hydroxide and a clear distinction based on the consideration which is gamma-oxy-cobalt hydroxide and was described until now On a false target (geometry target), by the about 6 way crystal system, more strictly Hexagonal, a prismatic crystal, It is the cobalt oxide which has the layer structure as belonged to one of monoclinic system crystal system and shown in drawing 3 . The grid is developing to c shaft orientations rather than c axial length of beta-Co (OH) 2 at least (specifically 5.5-7.0A), and the valence of cobalt reaches higher order than 3.0. And although it cannot become clear in detail, since it becomes the cause of main that the valence of cobalt reaches higher order than 3.0 etc. and electronic-conduction nature is discovered in the cobalt layer of a microcrystal, this oxide is

considered with conductivity higher than beta-oxy-cobalt hydroxide. For this reason, the utilization factor of a nickel hydroxide particle improves in the non-sintering positive electrode for alkaline batteries which made gamma-oxy-cobalt hydroxide the electric conduction agent.

[0081] Moreover, the electrochemistry behavior of gamma-oxy-cobalt hydroxide is shown by <u>drawing 6</u> or <u>drawing 8</u>, and shifts the potential of the charge and discharge of gamma/alpha system in this case in about 50-100mV and the **** direction compared with the charge-and-discharge system of conventional beta/beta. And such electrochemistry behavior of gamma-oxy-cobalt hydroxide is closely related to the capacity recovery factor after the short circuit preservation shown by 3. That is, since gamma-oxy-cobalt hydroxide has high conductivity, it maintains current collection from much nickel hydroxide at the time of short circuit preservation. Moreover, since the reduction potential in the inside of the alkali electrolytic solution is ** compared with beta-oxy-cobalt hydroxide as mentioned above while gamma-oxy-cobalt hydroxide has oxidized to the state where itself exceeds 3.0 **, the state (state dissolved into the electrolytic solution) of 2.0 ** is not returned easily. For this reason, destruction of the electric conduction network conventionally caused in the positive electrode when reduction progressed intensively in the section near the substrate skeleton at the time of short circuit preservation can be suppressed. in this way, in the non-sintering positive electrode for alkaline batteries which made gamma-oxy-cobalt hydroxide the electric conduction agent, compared with the conventional positive electrode, it is markedly alike, and the capacity recovery factor after high short circuit preservation is given

[0082] As mentioned above, the property of the non-sintering positive electrode for alkaline batteries shown by 3. and many physical properties of the gamma-oxy-cobalt hydroxide clarified by 4. can be associated clearly. In addition, although the high order cobalt oxide x shown above and y were observed in the state almost near single phase from the X diffraction That to which a part of beta-oxy-cobalt hydroxide exists an X diffraction result as a mixed phase in the gamma-oxy-cobalt hydroxide of KOH oxidization as shown in <u>drawing 9</u> (these) the difference in the delicate moisture content of alkali FANIKYURA formed at the time of oxidation treatment -- a cause -- being generated -- it checked in another experiment that the almost same positive-electrode property was acquired even if it uses for an electric conduction agent Furthermore, the thing to which Co 3O4 exists as a mixed phase slightly in the gamma-oxy-cobalt hydroxide of KOH oxidization although an X diffraction view is not shown, That to which a part of beta-oxy-cobalt hydroxide exists as a mixed phase in the gamma-oxy-cobalt hydroxide (Na type gamma-oxy-cobalt hydroxide) of NaOH oxidization, And Co 3O4 obtained the same experimental result also about three of thing **s which exist as a mixed phase slightly in the gamma-oxy-cobalt hydroxide of NaOH oxidization. That is, if gamma-oxy-cobalt hydroxide is a principal component, such some impurities will not have big influence on a positive-electrode property.

[0083] Moreover, some what sets the ideal structure expression to K(NiO2) 3, things set a little to difference nickel0.75K0.25OOH with this are in the reference about gamma-oxy-nickel hydroxide. An ideal structure expression with the same said of gamma-oxy-cobalt hydroxide: M(CoO2) 3 or Co0.75M0.25OOH (M is K or Na) If it thinks, the mole fraction of M/Co is expected to be 33% in an upper limit, and this is not so much separated from the actual measurement obtained in 4.1.1. or 4.2.1. However, the oxide of perfect ideal structure is not obtained rash. Each M/Co value of the gamma-oxy-cobalt hydroxide containing some above-mentioned impurities was about 20% (actual measurement). Therefore, if this ratio is in the range which is about 20 - 33%, it can be said that it does not change as a positive-electrode property.

[0084] Furthermore, although considered as the method of heating while mixing a cobalt hydroxide standard sample and the pulverized powder of an alkali granular reagent and sending air in the oxidization at the time of sample production of 1. In case this oxidizes the cobalt hydroxide (particle size is 0.2 micrometers, a BET specific surface area is 25m2/g, and the wettability to liquid is very large) of a particle independently, it is because it is the easiest at the point that this method makes alkali FANIKYURA suitable for oxidization. Therefore, the oxidation-treatment method of a Co(OH) 2 covering nickel particle (particle size differs from specific surface area, and the wettability to liquid completely differs) and the fine processing conditions which are shown in the following example 2 differ from the above.

[0085] (Example 2)

6. The Co(OH) 2 covering nickel particle used as the production raw material of a Co(OH) 2 covering nickel particle was produced in the following procedures. First, the nickel hydroxide solid-solution particle used as a mother particle was compounded using the following well-known technique. That is, the nickel sulfate was made into the principal component, and while aqueous ammonia adjusted Solution pH in the solution which only the specified quantity made contain a cobalt sulfate and a zinc sulfate, the sodium hydroxide was dropped gradually, and the method of depositing a spherical nickel hydroxide solid-solution particle was used. The nickel hydroxide solid-solution particle which deposited by this method was rinsed, and it dried, and considered as the mother particle.

[0086] Then, adjusting so that pH may maintain 12 at 35 degrees C, the aforementioned nickel hydroxide solid-solution particle was supplied in cobalt-sulfate solution, sodium-hydroxide solution was added gradually, and stirring was

continued, and on the solid-solution particle front face, cobalt hydroxide was deposited and was made into the Co(OH) 2 covering nickel particle. About the amount of covering of cobalt hydroxide, it adjusted here so that the ratio of the enveloping layer weight to the AUW of a Co(OH) 2 covering nickel particle might become 5.0 % of the weight. Co (OH)2 produced coated particle performed the vacuum drying, after rinsing.

[0087] The Co(OH) 2 covering nickel particle obtained here checked that a mean particle diameter was about 10 micrometers by measurement of a laser diffraction formula particle-size-distribution meter. It checked that the cobalt hydroxide of an enveloping layer had furthermore covered the whole particle surface with the thickness of about 0.1 micrometers from observation of a scanning electron microscope (SEM) and a transmission electron microscope (transverse electromagnetic). Moreover, the BET specific surface area of this particle was about 7m2/g.

[0088] 7. Oxidation treatment was performed to explanation of the oxidation-treatment 7.1. reactor to a Co(OH) 2 covering nickel particle, next the above-mentioned Co(OH) 2 covering nickel particle. First, the equipment used on the occasion of processing is explained in detail.

(Oxidation-treatment equipment) The general-view cross section of the oxidation-treatment equipment used for drawing 10 by this invention is shown. Heating keeping warm of the internal surface can be carried out by being the container of the product [1] made from stainless steel, and the lid of the product [2] made from stainless steel, and the jacket being attached in the wall surface by each, and letting hot water or steam pass in a jacket. Mixed stirring of the particle which supplied 3 to the agitator wing by the chopper wing, and supplied 4 in the container 1 is carried out. As 5 and 6 showed to the dotted line, the input of air is attached in these wing shanks, and the compressed air can be sent in in a container 1. 7 is a blast area and the air which passed along the bag filter of 8 can be discharged out of a container by opening the bulb 9 of the ** style. Although not shown in drawing here, the bag filter of 8 is equipped with the heating function for preventing dew condensation, and the particle payment chute function (pulse air method) for preventing blinding. 10 is a thermo-hygrometer and acts as the monitor of the damp or wet condition of the particle within a container by measuring the humidity of the mainly exhausted air. 11 is the dropping mouth which trickles alkali solution in a container, opens the dropping bulb 13 and supplies in a container the alkali solution of the specified quantity put into the liquid tank 12. 14 is a microwave generator and 15 is a waveguide which draws microwave in a container. Microwave is irradiated in a form as shown by the dotted-line arrow in drawing, and heats the particle in a container. Moreover, the output is adjusted by automatic control so that the microwave generator 14 may maintain the temperature which the indicated value of the contact process thermometer 16 (the temperature of a particle is measured) attached in the vessel-wall side set up. In addition, although not shown in drawing, each part grades including a blast area are shielded and protected in a metal mesh, in order to prevent leakage **** of the microwave out of equipment. 17 is a discharge charge which takes out the particle after processing.

[0089] (Oxidation-treatment equipment for comparison) The general-view cross section of the oxidation-treatment equipment (batch-process fluidized-bed-granulation equipment) used for drawing 11 as an object for comparison is shown. 18 is a cylinder-like equipment housing, and the wall surface of the cone-like section 19 under it is equipped with the jacket, and it can carry out heating keeping warm of the interior by letting hot water or steam pass in a jacket. 20 is a blower for sending in heating air in an equipment housing, and the heater for 21 heating air and 22 are piping which connects a housing with a blower. 23 is an impeller for stirring a particle and 24 is the straightening vane of the air current at the time of making a particle flow. 25 is a spraying nozzle for spraying alkali solution, and piping which transports the compressed air at the time of 26 spraying alkali solution, piping whose 27 transports alkali solution, and 28 are the tank which stores alkali solution, and a compressor which makes the compressed air. It is equipped with the particle payment chute function (pulse air method) for preventing blinding, although 29 is the bag filter which is made not to be discharged in the housing exterior and the particle does not show it in drawing, when a particle flows. 30 is piping and is connected to the fan of 31. Moreover, 32 is the thermometer of a contact process and can act as the monitor of the temperature of the particle which is flowing.

[0090] 7.2. As a procedure (active material of this invention) processor of heating oxidation treatment, the "microwave dryer FMD type" (tradename) made from Fukae Industry was used. Operation here is explained in detail using drawing 10 .

[0091] The inside of a container was kept warm by letting 110-degree C steam pass first in the jacket with which the wall surface of a container 1 and a covering device 2 was equipped, and 6.0kg of Co(OH) 2 covering nickel particles was supplied here. Next, the lid 2 was shut, and it is in a state [having opened], and the bulb 9 of the ** style rotated the agitator wing 3 and the chopper wing 4, carried out mixed stirring of the particle, and threw in the alkaline-water solution in the container from the dropping mouth 11. The alkaline-water solution used potassium-hydroxide solution (room temperature) of 45 % of the weight of concentration here, and the drip could be 700g. The dropping bulb 13 was closed after that, the mixture for about 3 minutes was continued, and the 1st process was ended.

[0092] At this 1st process, a particle turns into a humid particle of an almost uniform FANIKYURA state. Next, sever air supply and it is made have extracted the bulb 9 of the ** style and for the inside of a container to be airtight-ized

mostly, and mixture was continued, irradiating microwave (frequency of 2450MHz) from a waveguide 15, and the humid particle was heated. Although it was a humid particle at the end time of the 1st process, and it was already heated with the heat from a vessel-wall side and had become about 70 degrees C, even setting temperature (it is 110 degrees C in this case) was reached by continuing microwave irradiation for about 3 minutes. It acted as the monitor of the change of the above particle temperature with the contact process thermometer 16 attached in the container wall. The 2nd process is completed now.

[0093] Then, while opening the bulb 9 of the ** style, air (the temperature of 50 degrees C and humidity are 0.01kgH (s)2 O/kgdry-air) was sent in in the container from the shank 5 of an agitator wing, and the shank 6 of a chopper wing. About microwave, the indicated value of the contact process thermometer 16 also irradiated mixture of a humid particle in the meantime continuing, controlling to become fixed at 110 degrees C. When processing was performed for about 20 minutes in this state, the bone dry of the particle was carried out mostly, and it also completed the reaction. In addition, about the judgment of the dryness of a particle, it carried out by acting as the monitor of the thermo-hygrometer 10 attached in the blast area. The 3rd process is ended above.

[0094] In this way, the obtained particle was the active material without a condensation grain tinctured with the indigo metallic luster to which the enveloping layer oxidized uniformly. This particle was taken out from the product discharge charge 17, rinsing for removing a superfluous alkali component and dryness were performed, and it considered as the positive active material. Most change of the color of the particle accompanying rinsing and dryness was not observed. Let this be the active material particle A.

[0095] Moreover, the active material particle B was produced as the same as the above except [all] using sodium-hydroxide solution instead of potassium-hydroxide solution. The metallic luster of this particle mist beam indigo blue was presented.

(Active material for comparison) On the other hand, oxidation treatment using the equipment for comparison was performed to the aforementioned Co(OH) 2 covering nickel particle. Here, the "new quince riser NQ type" (tradename) made from un-2 PAUDARU was used as equipment. Drawing 11 explains operation of oxidation treatment using this equipment in detail.

[0096] First, the inside of a housing was kept warm through 80-degree C hot water in the wall surface jacket of the cone-like section 19, and the 950g of the same Co(OH) 2 covering nickel particles as having used here in the example 1 was supplied. Then, the impeller 23 was rotated, the heater 21, the blower 20, and the fan 31 were operated, and the rise heat style was generated in the housing. Under the present circumstances, the hot blast which passed along the straightening vane 24 is made fluidized, heating the supplied Co(OH) 2 covering nickel particle. Thus, after the particle had flowed, alkali solution was sprayed using the spraying nozzle 25. As alkali solution, 25% of the weight of potassium-hydroxide solution was used, and the amount of spraying was set to 200g in 10 minutes here. By the time it finishes spraying, alkali solution will permeate on the surface of a particle, and the cobalt hydroxide of an enveloping layer becomes a high order oxide by operation with hot blast. After the spraying end, the particle was made to flow in hot blast about further 15 minutes, and processing was completed. It acted as the monitor of the particle temperature with the contact process thermometer 32, and hot blast conditions etc. were operated so that processing temperature might serve as the set point (80 degrees C in this case) during operation of these series. Then, equipment was stopped, the particle was taken out from the housing, rinsing and dryness for removing superfluous alkali were performed, and it considered as the positive active material. Let this be the active material particle C. In addition, this particle presented black.

[0097] Moreover, the positive active material D was produced as the same as the above except [all] using sodium-hydroxide solution instead of potassium-hydroxide solution. This active material presented dark brown.

8. In order to check many properties of production of a cell, and the positive active material of A-D obtained by the evaluation above-mentioned technique, the procedure described below performed production and evaluation of a cell. First, the pure water of a proper quantity was added to each of sample A-D, the active material paste was adjusted, and only the specified quantity filled up the foaming nickel porous-body substrate with a% [of porosity] of 95, and a thickness of 1.3mm with this active material paste. Then, after drying this within a 80-degree C dryer, it rolled out in thickness of about 0.7mm using the roll press, cutting processing of this was carried out further at the predetermined size, and the nickel positive electrode corresponding to four sorts of active material A-D was produced.

[0098] About these four sorts of nickel positive electrodes, the nickel-hydrogen battery of nominal capacity 1600mAh was produced in 4 / 5A sizes by the well-known method using the alkali electrolytic solution which made the principal component a hydrogen storing metal alloy negative electrode, the polypropylene nonwoven fabric separator which performed hydrophilicity-ized processing, and the potassium hydroxide (7-8N). About each cell, the utilization factor of each positive electrode was measured by the method shown by ** in an example 1. Furthermore, the method shown in following ** estimated the capacity recovery factor after short circuit preservation of each positive electrode.

[0099] ** The capacity of 5 cycle repeat and 5 cycle eye was measured for the cycle made to discharge until it charges

by charge rate 1CmA first for 1.2 hours and a cell voltage is set to 1.0V by electric discharge rate 1CmA about the cell which evaluation of capacity recovery-factor ** after short circuit preservation ended. Then, this cell was short-circuited with the electric resistance of 1 ohm, and it saved under 45-degree C atmosphere. About the period saved here, it considered as three levels for three days (short period), two weeks (middle), and one month (long period of time), and carried out using a cell different, respectively. The capacity of 5 cycle repeat and 5 cycle eye was measured for the cycle made to discharge until it charges by charge rate 1CmA again for 1.2 hours and a cell voltage is set to 1.0V by electric discharge rate 1CmA about the cell after preservation. From the above measurement result, the capacity recovery factor after the short circuit preservation in three retention periods of each positive active material was computed by carrying out division process of the value of the cell capacity after short circuit preservation by the cell capacity before short circuit preservation.

[0100] The evaluation result about each positive active material is shown in (Table 4).

[0101]

[Table 4]

正極活物質 の種類	利用率 [%]	短絡保存後の容量回復率[%]		
		3日(短期)	2週間(中期)	1ヶ月(長期)
A	105.8	99.7	99.2	98.4
B	105.9	99.6	99.3	98.9
C	98.2	99.2	93.3	90.6
D	99.1	98.2	91.1	88.6

[0102] The positive active materials A and B obtained by oxidation treatment mainly concerned with the microwave heating of this invention have a utilization factor higher than the comparison active materials C and D, and the value becomes large rather than 100%. That is, the charge-and-discharge reaction of nickel hydroxide becomes larger than 1 electronic reaction. Moreover, A and B are superior to C and D also about the capacity recovery factor after short circuit preservation, and the difference is remarkable at especially the case of a mothball. This suggested that there was a remarkable difference to the physical properties of the cobalt oxide with which the current collection performance of the electric conduction network of a positive electrode in which the active material particles A and B were used is considered because it improved further rather than C and D, and forms the enveloping layer between the active material particles of A-D simultaneously etc. Then, in order to clarify this cause, powder analysis described below was performed about the cobalt oxide considered to relate to the four above-mentioned sorts of active material particles, and these.

[0103] 9. Analysis of Powder Analysis 9.1. Active Material Particle (the 1)
First, in order to clarify the difference in the color of active material particle A-D observed with the naked eye at the time of an experiment, the colorimetry based on a diffuse reflection method was carried out using the spectral-colorimetry meter (Minolta Camera CM- 3500d). On the occasion of measurement, each active material particle was measured here in the powdery state, without putting in, pushing and hardening sufficient amount for the petri dish for fine-particles sample measurement (Minolta Camera CM-A128). (In addition, even if it pushes and hardens, a spectrum hardly changes.) A setup of terms and conditions was carried out as follows.

[0104] Light-receiving [lighting /] optical system: d/8 (diffused lighting and the direction light-receiving of 8 degree), S C E (mirror reflection light removal)
light source: -- D65 visual field: -- diameter of 10-degree measurement: -- the diameter of about 30mm (target mask CM-A127 for the Minolta Camera petri dishes is used)
The reflected light with a petri dish was excepted using proofreading glass (Minolta Camera CM-A129).

[0105] The measurement result of a reflectance spectrum is shown in drawing 12 . As for the active material particles A and B of this invention discriminated when it had indigo metallic luster with the naked eye, a reflection factor shows the maximum of a reflection factor near the wavelength of 450nm highly (that is, migrating to the whole region bright) over the whole region. (For this reason, it looks indigo.) The comparison active material C discriminated as it is black with the naked eye has a low reflection factor covering the whole region, and the comparison active material D discriminated from dark brown with the naked eye has strong reflection of the red field where wavelength is large. Thus, if this technique is used, it can quantify clearly also about the difference in the color of the delicate particle felt with the naked eye.

[0106] The following two possibility can be considered as a cause which shows a difference of the above colors here.
(1) The particle size and specific surface area of an active material particle, and the further are reflecting the difference among particle shapes, such as a covering state of a cobalt oxide layer.
(2) The difference in the electronic state of the cobalt oxide which forms a particle enveloping layer is reflected.

[0107] Then, in order to investigate about the possibility of (1) first, Co distribution state of the particle front face and cross section by measurement (a laser diffraction formula particle-size-distribution meter is used) of particle size and

particle size distribution, measurement (BET adsorption method) of specific surface area, observation on the front face of a particle by the scanning electron microscope (SEM), observation of the particle cross section by the transmission electron microscope (transverse electromagnetic), and the electron ray probe microanalyzer (EPMA) was observed about four sorts of active material particle A-D. Consequently, a difference was hardly observed by the covering state of the particle size and specific surface area of an active material particle, and a cobalt oxide layer etc. by A-D, but, as for each of each active material particles, the mean particle diameter had the same particle size distribution by 10 micrometers, and the surface checked that the whole surface was completely covered with the cobalt oxide with a thickness of about 0.1 micrometers. Therefore, the difference in the color of an active material particle is not based on the reason of the above (1), and judged that it was based on the reason of (2).

[0108] The difference should be looked at by the value of the electrical conductivity of an active material particle if the cause of a difference of the color of an active material particle reflects the difference in the electronic state of the above (2), i.e., the cobalt oxide which forms a particle enveloping layer. Next, in order to check this point, the active material particle of each A-D was fabricated on the pellet, and electrical conductivity was measured using the direct-current 4 terminal method. Consequently, the value of electrical conductivity had A and almost equal B, and became the order of A-B>C>D, and the active material particles A and B which presented indigo blue all showed the value of 10 times or more compared with D of about 5 times and dark brown compared with black C. Therefore, the active material particle (active material particle to which the spectral reflectance in the visible whole region is size, and had the maximal value of 4.0% or more of spectral reflectances in the wavelength of about 450nm rather than 3.5% when saying concretely) which presents indigo blue as the difference in the color of said particle reflected the difference in the electronic state of the cobalt oxide which forms an enveloping layer and shown by drawing 12 has the very high electronic-conduction nature of a cobalt oxide. For this reason, the utilization factor of a positive electrode is raised greatly. In addition, by the cell produced using active materials A and B, after performing the charge and discharge of a number cycle, it checked that the colorimetry result whose active material particle (what was rinsed and dried) which disassembled the cell and was separated from the positive electrode also presented indigo blue, and described it above too was obtained. That is, when carrying out the charge-and-discharge reaction of nickel hydroxide within a cell, there is no change in the electronic state of the cobalt oxide which forms an enveloping layer so much, and high electronic-conduction nature is held.

[0109] Then, the X diffraction was measured in order to clarify structure of the cobalt oxide which forms the enveloping layer of the aforementioned active material particle. However, like point **, since this enveloping layer covered the front face of a particle with the very thin thickness of about 0.1 micrometers, the diffraction diagram became a thing only reflecting the nickel hydroxide which is a mother particle on parenchyma, and the diffraction peak relevant to the cobalt oxide which forms an enveloping layer has not been observed to satisfaction. Then, the cobalt hydroxide standard sample prepared in the previous example 1 was put on the coexistence atmosphere of a potassium hydroxide or a sodium hydroxide, water, and air (oxygen), and was oxidized on various conditions, and the color by X diffraction measurement and the spectral-colorimetry meter was measured.

[0110] 9.2. gamma-oxy-cobalt hydroxide of the consideration **KOH oxidization based on the analysis of various cobalt oxides, and it : the production method is as having described into the example 1, and an X diffraction view is drawing 1 . Presenting indigo metallic luster, the reflectance spectrum by the spectral-colorimetry meter is drawing 13 . Below, the cobalt oxide [this] x is written like the time of an example 1.

[0111] ** gamma-oxy-cobalt hydroxide of NaOH oxidization : the production method is as having described into the example 1, and an X diffraction view is drawing 7 . Presenting indigo metallic luster, the reflectance spectrum by the spectral-colorimetry meter is drawing 14 . Below, the cobalt oxide [this] y is written like the time of an example 1.

** CoO (OH)

(3-1) A crystalline high thing (namely, CoHO2) : the oxide which heat-treated cobalt hydroxide at 80 degrees C for 15 hours after sinking into 3% of the weight of sodium-hydroxide solution, and was obtained. Below, the cobalt oxide [this] z is written. The X diffraction view measured after rinsing and drying after processing is shown in the upper case of drawing 15 . The color of the oxide z observed with the naked eye is brown, and shows the reflectance spectrum by the spectral-colorimetry meter in drawing 16 . In measurement by the titrimetric method described into the example 1, the cobalt valence was checked with 2.98.

[0112] (3-2) A crystalline low thing (namely, beta-CoOOH) : the oxide which heat-treated cobalt hydroxide at 80 degrees C for 6 hours after sinking into 25% of the weight of sodium-hydroxide solution, and was obtained. Below, the cobalt oxide [this] u is written. The X diffraction view measured after rinsing and drying after processing is shown in the lower berth of drawing 15 . Although only the field (003) diffraction peak which should originally be near the 20 degree (4.4A) shifts a little and is observed near the 19 degree (4.6A), the fundamental diffraction pattern is the same as Oxide z. At present, the cause of this shift cannot be made clear in detail. The color of the oxide u observed with the naked eye is black, and the reflectance spectrum by the spectral-colorimetry meter is shown in drawing 16 . In

measurement by the titrimetric method described into the example 1, the cobalt valence was checked with 2.91.

[0113] ** Co 3O4 : the oxide which heat-treated cobalt hydroxide at 100 degrees C for 6 hours after sinking into 30% of the weight of sodium-hydroxide solution, and was obtained. Below, the cobalt oxide [this] v is written. The X diffraction view of the sample measured after rinsing and drying after processing is drawing 17 . Compared with the thing of the reagent generally marketed as Co 3O4, crystallinity is quite a low. The color of the oxide v observed with the naked eye is black, and the reflectance spectrum by the spectral-colorimetry meter is drawing 18 . In measurement by the titrimetric method described into the example 1, the cobalt valence was checked with 2.62. Moreover, when a potassium hydroxide was used instead of a sodium hydroxide, it checked that the almost same thing was obtained.

[0114] When the five above-mentioned cobalt oxides were fabricated on the pellet, respectively and electrical conductivity was measured using the direct-current 4 terminal method, the value had x and almost equal y, and it was the order of x-y>u>v>z. That is, gamma-oxy-cobalt hydroxide (Oxide x and y) has high electronic-conduction nature [else]. This is considered because it became the cause of main that the valence of cobalt reaches higher order than 3.0 etc. and electronic-conduction nature was discovered to the cobalt oxide.

[0115] Next, the reflectance spectrum by the spectral-colorimetry meter observed by gamma-oxy-cobalt hydroxide: Consider drawing 13 and drawing 14 (a color called indigo metallic luster). Fundamentally, since these spectrums are the things based on powdered diffuse reflection, as a ** type is shown in drawing 19 , the light a reflected on the crystal front face and the light b which penetrated the inside of a crystal are put together, and they are measured as the principle. And according to the diffuse reflection method, in the transition-metals compound which has an absorption band with a large absorbance in a visible region, it is known that selective reflection of the light of the absorption band will be carried out very strongly (getting it blocked and the reflected light a becoming a thing near the absorption spectrum of a compound), and this light will be observed. (Although its transmitted light can be seen and potassium permanganate:KMnO4 which has a strong absorption band by charge transfer changes in a green field (530nm) as a typical example is visible to a purplish red color (green complementary color) if it is solution, as a fine crystal, selective reflection of the light of the green field which is an absorption band is carried out strongly, and it is visible to the green tinctured with gloss.) And the reflection factor maximum of a diffuse reflectance spectrum arises to this green field. Here, in J.Electrochem.Soc. and 136 (1989) 613-619., gamma-oxy-nickel hydroxide has an absorption band strong against a field with a wavelength of 450nm (indigo), this belongs to the charge transfer changes between metal-oxygen, and D.A.Corrigan and others expresses the judgment that it relates to existence of the tetravalent nickel kind in gamma-oxy-nickel hydroxide further. Therefore, if a gamma-oxy-nickel hydroxide pair is carried out temporarily and spectrum measurement by the diffuse reflection method is performed, the maximum of a reflection factor will appear in a field with a wavelength of 450nm by the above-mentioned principle, and it may become the proof this indicates existence of a tetravalent nickel kind to be.

[0116] Although becoming clear to details was not completed at present based on the above consideration, this invention persons interpreted it as that to which the absorption band based on the charge transfer changes between metal-oxygen exists in about 450nm like gamma-oxy-nickel hydroxide also in gamma-oxy-cobalt hydroxide. Since this absorption band has the large absorbance, according to the diffuse reflection method, selective reflection of the about 450nm corresponding light will be carried out very strongly, and it brings a color called indigo metallic luster to this oxide. And this is quantitatively expressed with drawing 13 and drawing 14 as the reflection factor maximum which put the mark. Furthermore, if above D.A.Corrigan's and others interpretation teaches, it can also be said that this result is reflecting existence of the tetravalent cobalt kind which exists in gamma-oxy-cobalt hydroxide.

[0117] Furthermore, it is thought that the cobalt oxide which forms the enveloping layer of the active material particles A and B of this invention made gamma-oxy-cobalt hydroxide the principal component when the survey result that each of similarity of the maximum position of the reflection factor of the reflectance spectrum (A in drawing 12 , B) of the active material particles A and B and the reflectance spectrum (drawing 13 and drawing 14) of gamma-oxy-cobalt hydroxide and these had very high electronic-conduction nature was doubled. Moreover, it is guessed that the cobalt oxide which forms the enveloping layer of the active material particles C and D for comparison mentioned above from the same consideration is the oxide of 3.0 or less **s which is equivalent to z, u, and v which were shown above.

[0118] Moreover, it is thought that it is based on the difference in the manufacture method for oxidation-treatment equipment that the difference arose as mentioned above in the oxidation state of the cobalt oxide which forms an enveloping layer. As mentioned above, two reaction processes are guessed by oxidation reaction of the enveloping layer of a Co(OH) 2 covering nickel particle, and the degree of completion of oxidization changes with the water in a system, and the states of oxygen (air) to it a lot also in which process. and the particle which became FANIKYURA by having an alkaline-water solution in a front face in order to have enlarged the degree of completion of this oxidization -- comparatively -- an elevated temperature -- it is important to lead to a bone dry over a certain amount of time from under humid environment

[0119] In the manufacture method for comparison (method using batch-process fluidized-bed-granulation equipment),

although it is necessary to send in a lot of hot blast at any time and and is fluidizing in order to make a particle fluidize therefore, the area with which an alkali humid particle touches air becomes large, and dryness of the alkaline-water solution from a particle front face is very early. That is, before the reaction of said process 1 and process 2 fully advances, the inclination for the alkaline-water solution on the front face of a particle to be drained is strong. Therefore, although it is easy to suppress generating of a particle lump accompanying processing, adhesion of the particle to an equipment wall, etc., it becomes difficult to oxidize a cobalt hydroxide enveloping layer to a completely high order state. Considering the above viewpoint, an alkaline-water solution attains the manufacture method of this invention to an elevated temperature quickly in order to use microwave as the heating technique, and it can make inevitably the suitable environment for advance of processes 1 and 2 where the amount of oxygen was also fully secured by heat and high humidity. By controlling by the form which described such environment above, a cobalt hydroxide enveloping layer receives oxidization completely, and reaches even gamma-oxy-cobalt hydroxide higher order than 3.0 **.

[0120] As mentioned above, according to the manufacture method shown by this invention, it is. The enveloping layer of a Co(OH)2 covering nickel particle is efficiently convertible for gamma-oxy-cobalt hydroxide.

9.3 Analysis of Active Material Particle (the 2)

Then, the active material particles A and B of this invention were dissolved in the acid, and the amount of the alkali metal (a potassium or sodium) contained in an active material using ICP AEM was measured. Moreover, it checked performing cross-section observation of an active material particle by the electron ray probe microanalyzer (EPMA), and alkali metal existing only in the enveloping layer section by the active material particles A and B, and not existing in an internal mother particle. As mentioned above, the measured value of the aforementioned ICP AEM is reflecting the amount of the alkali metal contained in the cobalt oxide which forms the enveloping layer as it is. It was about 27, when the amount of alkali metal contained in the cobalt oxide which forms the enveloping layer of the active material particles A and B was estimated based on this point and all set molar quantity of a cobalt atom to 100. These analysis results are not contradictory in the aforementioned guess that the cobalt oxide which forms the enveloping layer of the active material particles A and B makes gamma-oxy-cobalt hydroxide a principal component.

[0121] Next, in order to grasp the electrochemistry behavior of the active material particle of this invention, the active material particles A and C were filled up with and pressed, respectively, it considered as the test electrode at the 1cmx1cm foaming nickel porous-body substrate which welded lead wire, and the cyclic voltammetry (valve flow coefficient) was measured on condition that the following.

Electrolytic solution: What added LiOH-H2O by the ratio of 40 g/l in KOH solution of 31 % of the weight of concentration (20-degree C specific gravity 1.31 g/l)

Counter electrode: Hydrogen storing metal alloy negative electrode (what was made to carry out charge and discharge combining another nickel hydroxide electrode beforehand, and was fully activated)

reference pole: -- Hg/HgO sweep condition: -- for +600mV (oxidization side) - -800mV (reduction side) after sweeping from immersing potential to +600mV -- operation Trace-speed ambient temperature of 3mV/second: The result related with two 20-degree-C active material particles is doubled, and it is shown in drawing 20 . Here, the reduction-current peak near +300mV corresponds to charge (oxygen evolution is also concurred with) of the nickel hydroxide whose sharp oxidation-current peak in electropositive potential is a mother particle rather than +400mV at electric discharge of nickel hydroxide. Therefore, although the peak which described a, b, and the sign is equivalent to the charge-and-discharge peak of the cobalt oxide of an enveloping layer, with the cobalt oxide in the active material particle A of this invention, about 50-100mV and oxidation reduction potential shift in the **** direction compared with the thing of the comparison active material particle C so that more clearly than drawing. When the experiment with the same said of the active material particle B was conducted, it checked that the same result as the active material particle A was shown. Such behavior is completely the same as the behavior of drawing 6 or drawing 8 shown in the example 1, and it is proved strongly that the cobalt oxide which forms the enveloping layer of the active material particles A and B also from this point makes gamma-oxy-cobalt hydroxide a principal component.

[0122] 10. The cobalt oxide of the physical properties of this invention active material particle and a positive-electrode property which forms the enveloping layer of the active material particles A and B of this invention as the relation above was carried out makes gamma-oxy-cobalt hydroxide a principal component. Since it becomes the cause of main that the valence of cobalt reaches higher order than 3.0 etc. and electronic-conduction nature is discovered, gamma-oxy-cobalt hydroxide has conductivity higher than oxides, such as beta-oxy-cobalt hydroxide. For this reason, the non-sintering positive electrode for alkaline batteries using the active material particles A and B of this invention has a utilization factor higher than what used the comparison active material particles C and D. In addition, since the start material of the active material particles A and B is a Co(OH)2 covering nickel particle, it is thought of because the effect of following (1) and (2) showed up that the utilization factor of a positive electrode using these active material particles A and B becomes higher than the utilization factor of a positive electrode using x in an example 1 and y.

[0123] (1) Since the dispersibility of the cobalt oxide which is an electric conduction agent was high, the current

collection from many nickel hydroxide solid-solution particles in the position distant from the substrate frame in a positive electrode was able to be maintained.

(2) The interface of the nickel hydroxide solid-solution particle of a mother particle and an enveloping layer was joined at the time of oxidation treatment, and the current collection from each solid-solution particle became is easy to be carried out.

[0124] Moreover, since the gamma-oxy-cobalt hydroxide which forms the enveloping layer of the active material particles A and B has high conductivity, it maintains current collection from much nickel hydroxide at the time of short circuit preservation. Furthermore, since the potential of charge and discharge has shifted gamma-oxy-cobalt hydroxide in about 50-100mV and the **** direction compared with the conventional cobalt oxide while it has oxidized to the state where itself exceeds 3.0 **, the state (state dissolved into the electrolytic solution) of 2.0 ** is not returned easily. For this reason, in the conventional positive electrode, destruction of the electric conduction network caused when reduction progressed intensively in the section near the substrate frame at the time of short circuit preservation can be suppressed. in this way, in the non-sintering positive electrode for alkaline batteries using the active material particles A and B, compared with a positive electrode, it is markedly alike conventionally, and the capacity recovery factor after high short circuit preservation is given

[0125] As mentioned above, the property of the non-sintering positive electrode for alkaline batteries shown by 8. and many physical properties of the active material particles A and B clarified by 9. can be associated clearly. In addition, JP,8-148145,A etc. has some publications about the pore distribution which an active material particle has. In the meaning which clarifies a relation with the active material particle of this invention, the pore distribution measurement result performed in the BET adsorption method of active material particle A-D used in the above-mentioned example is shown in (Table 5).

[0126]
[Table 5]

正極活物質の種類	作製条件など	直径６０Å以上の細孔空間の割合
A	本発明のKOHaq共存酸化	18.5%
B	本発明のNaOHaq共存酸化	17.9%
C	比較のKOHaq共存酸化	22.5%
D	比較のKOHaq共存酸化	19.7%

[0127] Publication that it is important that 20% or more of the total pore-space total volume which exists in an active material particle is occupied by pore with a diameter of 60A or more because of the improvement in a utilization factor is in a previous official report. Fundamentally, the active material particles A and B of this invention do not correspond to the above-mentioned publication so that more clearly than (Table 5). However, even if it produced a sample to which a pore distribution corresponds to the above-mentioned publication intentionally (this is producible if either the synthetic conditions of a Co(OH) 2 covering nickel particle or subsequent oxidation-treatment conditions are changed.), the improvement in a remarkable utilization factor was not accepted. From this, I think that there is especially no relevance of a pore distribution and a utilization factor of an active material particle this invention persons were indicated to be in the previous official report.

[0128] Moreover, although enveloping layer formation by the liquid phase process was performed on the occasion of production of a Co(OH) 2 covering nickel particle in this example The covering conditions in that case etc. are not what is limited to what was described here. Moreover, a nickel hydroxide solid-solution particle and cobalt hydroxide powder are mixed, and even if it uses the method (machine alligation) of making a particle front face covering with cobalt hydroxide using the shearing force and impulse force at the time of machine mixture etc., the active material particle of this invention is producible.

[0129]
[Effect of the Invention] As explained above, the positive active material consists of solid-solution particles which carried out the principal component in the high order cobalt oxide which made gamma-oxy-cobalt hydroxide the principal component, and nickel hydroxide, the alkaline battery of this invention has very high order gamma-oxy-cobalt hydroxide, and the alkaline battery [after neglect in an overdischarge or the short circuit state, and a mothball or hot preservation] which can maintain high capacity can be offered, attaining a high positive-electrode utilization factor, since it has high conductivity.

[Translation done.]